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16. ABSTRACT

A national emission standard for sulfur dioxide and reduced sulfur compound emissions from petroleum refinery sulfur recovery plants is being proposed under authority of section 111 of the Clean Air Act. Sulfur dioxide is a criteria pollutant whose adverse effects are well documented. Reduced sulfur compound emissions could reach ambient levels sufficient to produce severe odor problems in the vicinity of a petroleum refinery in the absence of the standard. The purpose of the proposed standard is to minimize reduced sulfur and sulfur dioxide emissions from refinery sulfur recovery plants to the level attainable with best available control technology. The standard will have the effect of reducing emissions from a typical refinery sulfur recovery plant by 99.9%. Environmental impact and economic impact statements quantifying the impacts of the proposed standard and alternative control options are included in the document.

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STANDARDS SUPPORT
AND
ENVIRONMENTAL IMPACT STATEMENT
VOLUME 1: PROPOSED STANDARDS OF PERFORMANCE FOR PETROLEUM REFINERY SULFUR RECOVERY PLANTS

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Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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Emission Standards and Engineering Division

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Standards Support and Environmental Impact Statement

Petroleum Refinery Sulfur Recovery Plants

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1. SUMMARY

1.1 PROPOSED STANDARDS

Standards of performance for new or modified sulfur recovery plants within petroleum refineries are being proposed under section 111 of the Clean Air Act. Depending on the type of emission control system installed to comply with these standards, residual emissions released to the atmosphere will consist of sulfur dioxide (SO_2) or reduced sulfur compounds, i.e. hydrogen sulfide (H_2S), carbonyl sulfide (COS) and carbon disulfide (CS_2), (see discussion below). The standards, therefore, limit either the concentration of SO_2, or the concentration of H_2S and the total concentration of H_2S, COS and CS_2, in the gases discharged into the atmosphere from new or modified refinery sulfur recovery plants. Specifically, emissions are limited to either 0.025 percent by volume of SO_2 on a dry basis and zero percent oxygen, or 0.0010 percent by volume of H_2S and 0.030 percent by volume of reduced sulfur compounds on a dry basis and zero percent oxygen.

The standards also require continuous monitoring of the concentration of SO_2 or H_2S and reduced sulfur compounds in the gases discharged into the atmosphere. This is to ensure proper operation and maintenance of the emission control systems.

1.2 ENVIRONMENTAL/ECONOMIC IMPACT

Two alternative emission control systems were considered to serve as the basis for standards of performance (i.e. best system of emission reduction, considering costs) for refinery sulfur recovery plants; the low-temperature extended Claus reaction system (alternative I) and various tail gas scrubbing systems (alternative II).

The alternative II systems consist either of oxidation-scrubbing processes or reduction-scrubbing processes. The oxidation-scrubbing processes first convert emissions from a refinery sulfur plant to SO_2 and then control these emissions with an SO_2 tail gas scrubbing system. The reduction-scrubbing processes convert emissions from a refinery sulfur plant to H_2S and then control these emissions with an H_2S scrubbing system. In some cases, the reduction-scrubbing processes are also followed with an incinerator. Thus, residual emissions released to the atmosphere from the oxidation-scrubbing processes and the reduction-scrubbing processes which are followed by incineration consist of SO_2. Residual emissions released to the atmosphere from the reduction-scrubbing systems which are not followed by incineration, however, consist of H_2S, COS and CS_2.

The potential environmental and economic impacts associated with standards based on either alternative I or alternative II are summarized in Table 1. There are no impacts associated with alternative I, since the level of control specified in most state implementation plans to meet and maintain the NAAQS for SO_2 requires new refinery sulfur recovery plants to install an alternative I emission control system.

There are no adverse environmental impacts associated with the proposed standards, which are based on alternative II. These standards will, however, lead to a reduction in national SO_2 emissions by some 55,000 tons per year, and a reduction in national energy consumption by some 54 million kw-hr/yr (90,000 barrels of fuel oil) in 1980.

TABLE 1. Environmental and Economic Impacts of Alternative Standards

IMPACT ACTION	Air	Water Pollution	Solid Waste	Energy	Noise	Economic
Alternative I	0	0	0	0	0	0
Alternative II (Proposed Standards)	$+3^{xx}$	0	0	$+1^{xx}$	0	-1^{xx}
No Standards or Delayed Standards	0	0	0	0	0	0

Key:
+ Beneficial Impact
- Adverse Impact

0 No Impact
1 Negligible Impact
2 Small Impact
3 Moderate Impact
4 Large Impact

x Short-term Impact
xx Long-term Impact
xxx Irreversible Impact

The economic impact associated with the proposed standards is reasonable on both large and small refiners. This impact is, however, greater on small refiners than large refiners due to the "economies-of-scale." The standards could reduce the profitability (as measured by return on assets) of a large refiner by 0.15-1.5 percent, and that of a small refiner by 1.5-7.5 percent. To maintain their profitability, the large refiner would have to increase prices on petroleum products by only 0.05-0.3 percent, and the small refiner by only 0.2-1.0 percent.

1.3 INFLATIONARY IMPACT

The Agency's guidelines for developing an Inflationary Impact Statement are increased operating costs in the fifth year of more than $100 MM per year, or increased prices of more than 5 percent. The increased operating costs in the fifth year associated with the proposed standards are only $16 MM per year, and the potential increase in prices is less than 0.5 percent. Consequently, an Inflationary Impact Statement has not been prepared.

2. INTRODUCTION

Standards of performance under section 111 of the Clean Air Act are proposed and promulgated following a detailed investigation of air pollution control methods available to the affected industry and the impact of their costs on the industry. This document summarizes the information obtained from such a study of sulfur recovery in petroleum refineries. Its purpose is to explain in detail the background and basis of the standards and to facilitate analysis of these standards by interested persons, including those who may not be familiar with the many technical aspects of the industry. Copies of the "Standard Support and Environmental Impact Statement - Petroleum Refinery Sulfur Recovery Plants" may be obtained by writing to the Public Information Center (PM-215), Environmental Protection Agency, Washington, D.C. 20460. (Specify "Standard Support and Environmental Impact Statement - Petroleum Refinery Sulfur Recovery Plants.")

2.1 AUTHORITY FOR THE STANDARDS

Standards of performance for new stationary sources are developed under section 111 of the Clean Air Act (42 U.S.C. 1857c-6), as amended in 1970. Section 111 requires the establishment of standards of performance for new stationary sources of air pollution which ". . .may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare." The Act requires that standards of performance for such sources reflect ". . .the degree of emission limitation achievable through the application of the best system of emission reduction which (taking into account the cost of achieving such reduction) the Administrator determines has been adequately demonstrated." The standards apply only to stationary sources, the construction or modification of which commences after regulations are proposed by publication in the Federal Register.

Section 111 prescribes three steps to follow in establishing standards of performance.

1. The Administrator must identify those categories of stationary sources for which standards of performance will ultimately be promulgated by listing them in the Federal Register.
2. The regulations applicable to a category so listed must be proposed by publication in the Federal Register within 120 days of its listing. This proposal provides interested persons an opportunity for comment.
3. Within 90 days after proposal, the Administrator must promulgate standards with any alterations he deems appropriate.

Standards of performance, by themselves, do not guarantee protection of health or welfare: that is, they are not designed to achieve any specific air quality levels. Rather, they are designed to reflect best demonstrated technology (taking into account costs) for the affected sources. The overriding purpose of the collective body of standards is to maintain existing air quality and to prevent new pollution problems from developing.

Previous legal challenges to standards of performance have resulted in several court decisions[1,2] of importance in developing future standards. In these cases, the principal issues were whether EPA: (1) made reasoned decisions and fully explained the basis of the standards, (2) made available to interested parties the information on which the standards were based, and (3) adequately considered significant comments from interested parties.

Among other things, the court decisions established: (1) that preparation of an environmental impact statement is not necessary for standards developed under section 111 of the Clean Air Act because under this section EPA must consider any counter-productive environmental effects of a standard in determining what system of control is "best;" (2) in considering costs it is not necessary to provide a cost-benefit analysis; (3) EPA is not required to justify standards that require different levels of control in different industries unless such different standards may be unfairly discriminatory; and (4) it is sufficient for EPA to show that a standard can be achieved rather than that it has been achieved by existing sources.

Promulgation of standards of performance does not prevent State or local agencies from adopting more stringent emission limitations for the same sources. On the contrary, section 116 of the Act (42 U.S.C. 1857-D-1) makes clear that States and other political subdivisions may enact more restrictive standards.

Furthermore, in heavily polluted areas more stringent standards may be required under section 110 of the Act (42 U.S.C. 1857c-5) in order to attain or maintain national ambient air quality standards prescribed under section 109 (42 U.S.C. 1857c-4). Finally, section 116 makes clear that a State may not adopt or enforce less stringent new source standards than those adopted by EPA under section 111.

Although standards of performance are normally structured in terms of numerical emission limits where feasible, alternative approaches are sometimes necessary. In some cases physical measurement of emissions from a new source may be impractical or exorbitantly expensive. For example, emissions of hydrocarbons from storage vessels for petroleum liquids are greatest during storage and tank filling. The nature of the emissions (high concentrations for short periods during filling and low concentrations for longer periods during storage) and the configuration of storage tanks make direct emission measurement highly impractical. Therefore, a more practical approach to standards of performance for storage vessels has been equipment specifications.

2.2 SELECTION OF CATEGORIES OF STATIONARY SOURCES

Section 111 directs the Administrator to publish and from time to time revise a list of categories of sources for which standards of performance are to be developed. A category is to be selected ". . .if [the Administrator] determines it may contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare."

Considerable attention has been given to the development of a methodology for assigning priorities to various source categories. In brief, the approach that has evolved is as follows. Specific areas of emphasis are identified by considering the broad strategy of the Agency for implementing the Clean Air Act. Often, these "areas" are actually pollutants which are primarily emitted by stationary sources. Source categories which emit these pollutants are then evaluated and ranked taking into account such factors as (1) the level of emission control (if any) already required by State regulations; (2) estimated levels of control that might result from standards of performance for the source category; (3) projections of growth and replacement of existing facilities for the source category; and (4) the estimated incremental amount of air pollution that could be prevented, in a preselected future year, by standards of performance for the source category. An estimate is then made of the time required to develop a standard. In some cases, it may not be feasible to develop a standard immediately for a source category with a high priority. This circumstance might occur because a program of research and development is needed to develop control techniques or because techniques for sampling and measuring emissions may require refinement.

Selection of a source category for standards development leads to another major decision, determination of the types of sources or facilities to which standards will apply. A source category often has several facilities that cause air pollution. Emissions from some of these facilities may be insignificant or very expensive to control. An investigation of economics may show that, within the costs that an owner could reasonably afford, air pollution control is better served by applying standards to the most severe pollution problems. For this reason (or perhaps because there may be no adequately demonstrated system for controlling emissions from certain facilities), standards often do not apply to all sources within a category. For similar reasons, the standards may not apply to all air pollutants emitted by such sources. Consequently, although a source category may be selected to be covered by standards of performance, not all pollutants or facilities within that source category may be covered by the standards.

2.3 PROCEDURE FOR DEVELOPMENT OF STANDARDS OF PERFORMANCE

Congress mandated that sources regulated under section 111 of the Clean Air Act utilize the best system of air pollution control (considering costs) that has been adequately demonstrated at the time of their design and construction. In so doing, Congress sought to:

1. Maintain existing air quality
2. Prevent new air pollution problems, and
3. Ensure uniform national standards for new facilities.

Standards of performance, therefore, must (1) realistically reflect best demonstrated control practice; (2) adequately consider the cost of such control; (3) be applicable to existing sources that are modified as well as new installations; and (4) meet these conditions for all variations of operating conditions being considered anywhere in the country.

The objective of a program for developing standards of performance is to identify the best system of emission reduction which "has been adequately demonstrated (considering costs)." The legislative history of section 111 and the court decisions referred to earlier make clear that the Administrator's judgment of what is adequately demonstrated is not limited to systems that are in actual routine use. Consequently, the investigation may include a technical assessment of control systems which have been adequately demonstrated but for which there is limited operational experience. In most cases, determination of the "degree of emission limitation achievable" is based on results of tests of emissions from existing sources. This has required worldwide investigation and measurement of emissions from control systems. Other countries with heavily populated, industrialized areas have sometimes developed more effective systems of control than those used in the United States.

Since the best demonstrated systems of emission reduction may not be in widespread use, the data base upon which standards are developed may be somewhat limited. Test data on existing well-controlled sources is an obvious starting point in developing emission limits for new sources. However, since the control of existing sources generally represents retrofit technology or was originally designed to meet an existing State or local regulation, new sources may be able to meet more stringent emission standards. Other information, however, is also considered and judgment is necessarily involved in developing standards.

A process for the development of a standard has evolved. In general, it follows the guidelines below.

1. Emissions from existing well-controlled sources are measured.
2. Data on emissions from such sources are assessed with consideration for such factors as: (a) the representativeness of the source tested (feedstock, operation, size, age, etc.); (b) the age and maintenance of the control equipment tested (and possible degradation in the efficiency of control of similar new equipment even with good maintenance procedures); (c) the design uncertainties for the type of control equipment being considered; and (d) the degree of uncertainty that new sources will be able to achieve similar level of control.
3. During development of the standards, information from pilot and prototype installations, guarantees by vendors of control equipment, contracted (but not yet constructed) projects, foreign technology, and published literature are considered, especially for sources where "emerging" technology appears significant.

4. Where possible, standards are developed which permit the use of more than one control technique or licensed process.
5. Where possible, standards are developed to encourage (or at least permit) the use of process modifications or new processes as a method of control rather than "add-on" systems of air pollution control.
6. Where possible, standards are developed to permit systems capable of controlling more than one pollutant (for example, a scrubber can remove both gaseous and particulate matter emissions, whereas an electrostatic precipitator is specific to particulate matter).
7. Where appropriate, standards for visible emissions are developed in conjunction with concentration/mass emission standards. The opacity standard is established at a level which will require proper operation and maintenance of the emission control system installed to meet the concentration/mass standard on a day-to-day basis, but not require the installation of a control system more efficient or expensive than that required by the concentration/mass standard. In some cases, however, it is not possible to develop concentration/mass standards, such as with fugitive sources of emissions. In these cases, only opacity standards may be developed to limit emissions.

2.4 CONSIDERATION OF COSTS

Section 111 of the Clean Air Act requires that costs be considered in developing standards of performance. This requires an assessment of the possible economic effects of implementing various levels of control technology in new plants within a given industry. The first step in this analysis requires the generation of estimates of installed capital costs and annual operating costs for various demonstrated control systems, each control system alternative having a different overall control capability. The final step in the analysis is to determine the economic impact of the various control alternatives upon a new plant in the industry. The fundamental question to be addressed is whether or not a new plant would be constructed if a certain level of control costs will be incurred. Other aspects that are analyzed are the effects of control costs upon product prices and product supplies, and producer profitability.

The economic impact of a proposed standard upon an industry is usually addressed both in absolute terms and by comparison with the control costs that would be incurred as a result of compliance with typical existing State control regulations. This incremental approach is taken since a new plant would be required to comply with State regulations in the absence of a Federal standard of performance. This approach requires a detailed analysis of the impact upon the industry resulting from the cost differential that exists between a standard of performance and the typical State standard.

The costs for control of air pollutants are not the only control costs considered. Total environmental costs for control of water pollutants as well as air pollutants are analyzed wherever possible.

A thorough study of the profitability and price-setting mechanisms of the industry is essential to the analysis so that an accurate estimate of potential adverse economic impacts can be made. It is also essential to know the capital requirements placed on plants in the absence of Federal standards of performance so that the additional capital requirements necessitated by these standards can be placed in the proper perspective. Furthermore, it is necessary to recognize any constraints on capital availability within an industry as this factor also influences the ability of new plants to generate the capital required for installation of the additional control equipment needed to meet the standards of performance.

A consideration of the impact of these standards on inflation is of major importance. Any action which will add significantly to inflationary pressures is considered major and requires an inflationary impact statement.

2.5 CONSIDERATION OF ENVIRONMENTAL IMPACTS

Section 102(2)(c) of the National Environmental Policy Act (NEPA) of 1969 (PL 91-190) requires Federal agencies to prepare detailed environmental impact statements on proposals for legislation or other major Federal actions significantly affecting the quality of the human environment. The objective of NEPA is to build into the decision-making process of Federal agencies a careful consideration of all environmental aspects of proposed actions.

As mentioned earlier, in a number of legal challenges to standards of performance for various industries, the Federal Courts of Appeals have held that environmental impact statements need not be prepared by the Agency for actions under section 111 of the Clean Air Act. Essentially, the Federal Courts of Appeals have determined that "...Section 111 of the Clean Air Act, properly construed, requires the functional equivalent of a NEPA impact statement" in the sense that the criteria "...the best system of emission reduction," "...require(s) the Administrator to take into account counter-productive environmental effects of a proposed standard, as well as economic costs to the industry..." On this basis, therefore, the Courts "...establish(ed) a narrow exemption from NEPA for EPA determinations under section 111."[1,2]

In addition to these judicial determinations, the Energy Supply and Environmental Coordination Act (ESECA) of 1974 (PL 93-319) specifically exempts actions under the Clean Air Act from NEPA requirements. According to section 7(c)(1), "No action taken under the Clean Air Act shall be deemed a major Federal action significantly affecting the quality of the human environment within the meaning of the National Environmental Policy Act of 1969."

The Agency has concluded, however, that the preparation of environmental impact statements could have beneficial effects on certain regulatory actions. Consequently, while not legally required to do so by section 102(2)(c) of NEPA, environmental impact statements will be prepared for various regulatory actions, including standards of performance developed under section 111 of the Clean Air Act. This voluntary preparation of environmental impact statements, however, in no way legally subjects the Agency to NEPA requirements.

To implement this policy, a separate section is included in this document which is devoted solely to an analysis of the potential environmental impacts associated with the alternative standards considered for proposal and promulgation. Both adverse and beneficial impacts in such areas as air and water pollution, increased solid waste disposal and increased energy consumption are identified and discussed. Appendix B of this document outlines those sections or chapters which examine these potential environmental impacts in detail.

2.6 IMPACT ON EXISTING SOURCES

Standards of performance may affect existing sources in either of two ways. Section 111 of the Act defines a new source as "any stationary source, the construction or modification of which is commenced after the standards are proposed." Consequently, if an existing source is modified after proposal of the standards, with a subsequent increase in air pollution, it may be subject to standards of performance. Amendments to the general provisions of Subpart A of 40 CFR Part 60 clarifying the meaning of modification were promulgated on December 16, 1975 (40 FR 58416).

Second, promulgation of a standard of performance requires States to establish standards of performance for existing sources in the same industry under section 111(d) of the Act; unless the standard for new sources limits emissions of a pollutant for which air quality criteria have been (or will be) issued under section 108 or one listed as a hazardous pollutant under section 112.

If a State does not act, EPA must establish such standards. General provisions outlining procedures for control of existing sources under section 111(d) were promulgated in the Federal Register as Subpart B of 40 CFR Part 60 on November 17, 1975 (40 FR 58346).

2.7 REVISION OF STANDARDS OF PERFORMANCE

Congress was aware that the level of air pollution control achievable by any industry may improve with technological advances. Accordingly, section 111 of the Act provides that the Administrator may revise standards of performance from time to time. Although standards proposed and promulgated by EPA under section 111 are designed to require installation of the "...best system of emission reduction...(taking into account the cost)..." the standards are reviewed periodically. Revisions are proposed and promulgated as necessary to assure that the standards continue to reflect the best systems of emission control as they become available. Such revisions are not retroactive but apply to stationary sources constructed or modified after proposal of the revised standards.

2.8 REFERENCES

1. Portland Cement Association vs. Ruckelshaus, 486 F. 2nd 375 (D.C. Cir. 1973).

2. Essex Chemical Corp. vs. Ruckelshaus, 486 F. 2nd 427 (D.C. Cir. 1973).

3. SULFUR RECOVERY PLANTS IN PETROLEUM REFINERIES

Sulfur emissions from petroleum refining are a function of the sulfur content of the crude oil being processed, the complexity of the refinery and the refinery fuel sources. Various refinery processes produce process gas or "fuel" gas which can contain significant amounts of sulfur, mainly as hydrogen sulfide. To meet the standards of performance promulgated in March 1974 (39 FR 9308) limiting sulfur dioxide emissions from fuel gas combustion in petroleum refineries, or to satisfy state or local emission codes, and to reduce corrosion problems, refineries "sweeten" or remove hydrogen sulfide from the fuel gas before burning it in process heaters and boilers.

Hydrogen sulfide removal from fuel gas consists of scrubbing with solutions which absorb H_2S. Regeneration of the scrubbing solutions evolves a side stream of concentrated hydrogen sulfide with lesser amounts of carbon dioxide, water vapor and hydrocarbons, which is processed in an appropriate recovery facility such as a Claus sulfur plant to produce elemental sulfur.

Claus sulfur plants have long been established as effective technology for sulfur recovery from process gases in petroleum refineries. Claus sulfur capacity in U.S. refineries totalled 8000 long tons per day as of April 1973.[1] Sulfur dioxide emissions from Claus plants based on operation at two-thirds capacity and 92 percent recovery are estimated at 338,000 tons in 1973.

The rapid rate at which sulfur plants are being installed makes them attractive candidates for standard development. Forecasted increases in domestic petroleum refining capacity indicate that a significant growth rate in refinery sulfur recovery is forthcoming. Over 1000 LT/D or about 13% of existing refinery sulfur plant capacity was scheduled for completion during 1974.[2]

Refinery sulfur plants are currently located in 25 states.[3] Sizes range from 4 to 375 long tons/day (LT/D) with 65 LT/D being an average size plant. Sulfur plants scheduled for start-up in 1974-75 reflect the trend toward larger facilities, averaging 107 LT/D.[4]

3.1 PROCESSES AND EMISSIONS

As discussed previously, hydrogen sulfide gases are released during the regeneration of amine or other scrubbing solutions which are used to desulfurize refinery process or fuel gases. In addition, some H_2S is removed from process water by sour water strippers. Most refineries include facilities for steam stripping H_2S from sour water streams as part of the waste water treatment system. Where sulfur recovery is practiced, the off-gases from the stripper are normally routed to the sulfur recovery plant.

The Claus Process

The Claus process has been used almost exclusively in petroleum refineries to recover sulfur. The basic exothermic reactions for the Claus process are:

(1) $H_2S + 1/2\ O_2 \rightarrow H_2O + S$

(2) $H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$

(3) $2\ H_2S + SO_2 \rightleftarrows 3S + 2H_2O$

A typical two-stage Claus plant is shown in Figure 3-1.[5] Hydrogen sulfide gas enters the burner with sufficient air to convert all H_2S to sulfur. As much as 50 to 60 percent conversion of the hydrogen sulfide to sulfur takes place in the initial reaction chamber by Reaction (1).

Reaction (2) also takes place, forming SO_2. After cooling, condensing and removing sulfur, the gases are reheated by mixing with a portion of the gases bypassed around the sulfur condenser and introduced into the first catalytic converter where the Claus reaction (Reaction 3) occurs. From the first catalytic converter the effluent gas is cooled, sulfur condensed and removed, and the gases reheated again. The process is repeated in the second catalytic converter. If needed, additional catalytic stages may be added to remove H_2S as sulfur.

Some carbonyl sulfide (COS) and carbon disulfide (CS_2) are formed in the reaction furnace in the presence of carbon dioxide and hydrocarbons:

(4) $CO_2 + H_2S \rightleftarrows H_2O + COS$

(5) $COS + H_2S \rightleftarrows H_2O + CS_2$

(6) $CH_4 + 2S_2 \rightleftarrows CS_2 + 2H_2S$

Depending on the exact nature of the sour-gas feed stream and the operating conditions in the upstream reaction furnace and catalyst beds, combined COS and CS_2 levels as high as 5000 ppmv may exist in the tail gas.[6] Values of 600-1500 ppmv are more common, however.

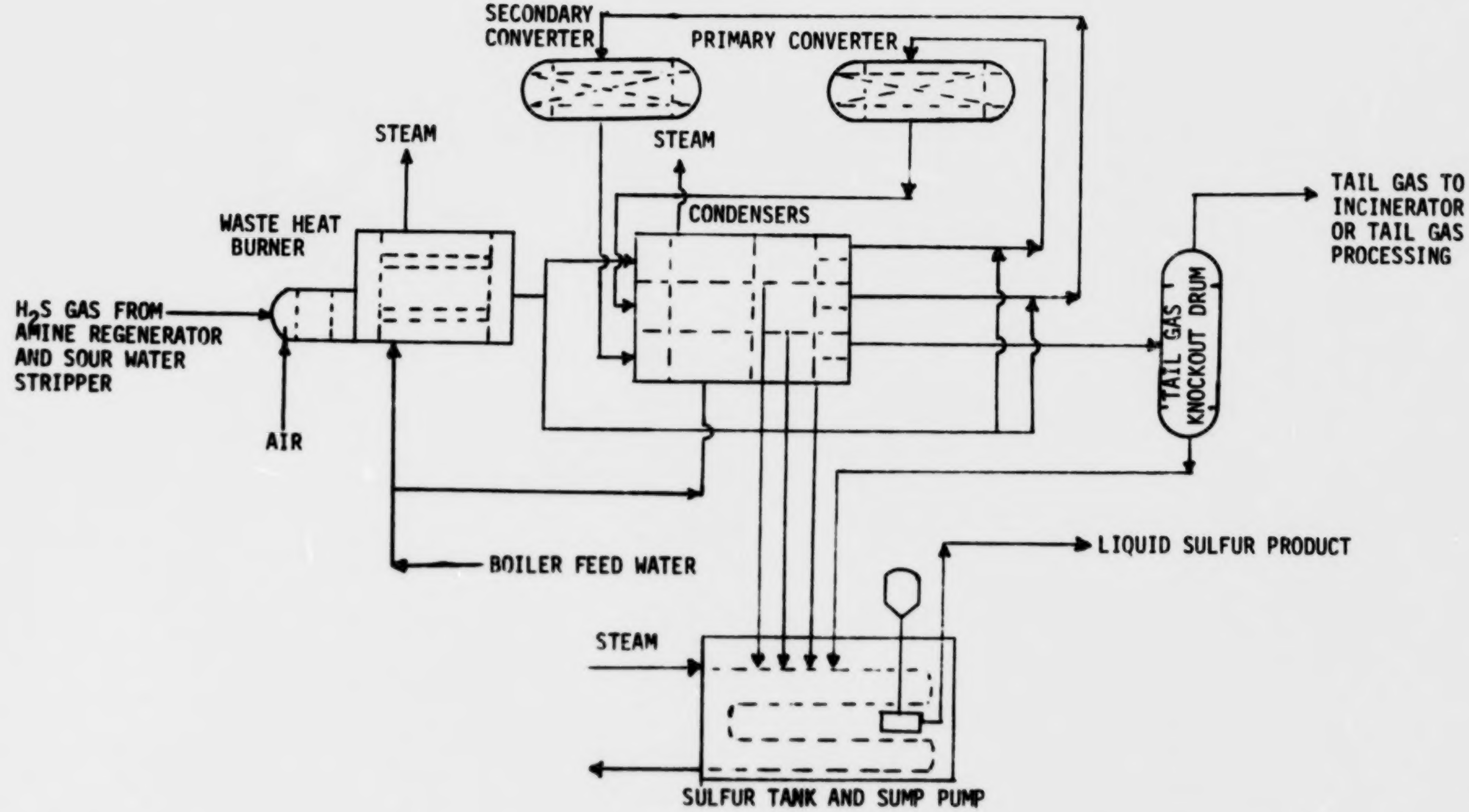
SECONDARY CONVERTER
PRIMARY CONVERTER
STEAM
STEAM
CONDENSERS
WASTE HEAT BURNER
H_2S GAS FROM AMINE REGENERATOR AND SOUR WATER STRIPPER
AIR
TAIL GAS TO INCINERATOR OR TAIL GAS PROCESSING
TAIL GAS KNOCKOUT DRUM
BOILER FEED WATER
LIQUID SULFUR PRODUCT
STEAM
SULFUR TANK AND SUMP PUMP

Figure 3-1. Typical packaged Claus plant (2 stage).[5]

The emissions of H_2S, SO_2, and sulfur vapor from Claus plants are directly dependent on the efficiency of sulfur recovery in the Claus plant. For example, a 100 LT/D Claus plant operating at 95 percent sulfur recovery efficiency would emit 5 LT/D sulfur in the form of H_2S, SO_2, sulfur vapor, COS and CS_2 formed in the reaction furnace. Gas stream compositions throughout a Claus plant are given in Table 3-1 for a hypothetical 100 LT/D plant operating at 95 percent recovery efficiency.[7]

Claus plant efficiencies in turn are dependent upon the following variables:[8,9,10]

(1) Number of catalytic conversion stages.

(2) Inlet feed stream composition.

(3) Operating temperatures and catalyst maintenance.

(4) Maintaining the proper stoichiometric ratio of H_2S/SO_2.

(5) Operating capacity factor.

For Claus plants fed with 90 mole percent H_2S, the sulfur recovery is approximately 85 percent for one catalytic stage and 95 percent for two or three stages. The percentage of sulfur recovery also increases with increasing concentration of the acid gas fed to the Claus plant. For plants having two or three catalytic stages, the sulfur recoveries for various acid gas concentrations are approximately 90 percent for a 15 mole percent H_2S feed stream, 93 percent for a 50 mole percent H_2S stream, and 95 percent for 90 percent H_2S concentration.[11]

Contaminants in the feed gas reduce Claus sulfur recovery efficiency. Hydrocarbons in Claus feedstocks require extra air for combustion. The

Table 3-1. TYPICAL COMPOSITION OF GAS STREAMS ENTERING AND LEAVING HYPOTHETICAL 100 LT/D REFINERY CLAUS PLANT
(Basis: sulfur recovery in Claus unit of 95 percent)

			Claus Tail Gas	
Composition (Vol. %)		Claus Intake	Before Incineration	After Incineration*
H_2S		89.9	0.59	--
SO_2		--	0.29	0.82
S_8 vapor and mist		--	0.05	--
COS		--	0.05	--
CS_2		--	0.04	--
CO		--	0.22	--
CO_2		4.6	0.86	2.05
HC (MW:30)		0.5	--	--
H_2		--	1.60	--
H_2O		5.0	20.60	20.40
N_2		--	75.69	76.54
O_2		--	--	0.18
Total		100.00	100.00	100.00
Temperature	°F	104	284	1200
Pressure	psia	21.3	18.5	Atm
Gas quantity Relative amount	mole	1	3.1	4.45
Flow	SCFM	2028	6,287	9,025

*Based on using 10 percent excess air in the incinerator and CH_4 as fuel.

added water and inert gas associated with burning hydrocarbons increases the size of the sulfur plant equipment and lowers sulfur recovery since the sulfur gas concentrations are decreased.[12] Higher-molecular-weight hydrocarbons in the feed also reduce Claus efficiencies because of soot formation on the catalyst.[13] High feedstock concentrations of CO_2 adversely affect catalyst life.[14]

Since the reactions in a Claus Plant are exothermic, sulfur recovery is enhanced by removing heat, hence operation at as low a temperature as practicable in the reactors without condensing sulfur vapor on the Claus catalyst is necessary. Sulfur recovery is also dependent upon catalyst performance. One vendor has reported a one to two percent loss in recovery efficiency over the period of catalyst life.[15] Catalyst life generally varies from 2 to 5 years depending on plant operation and contaminants in the feedstock discussed previously.

Deviation above or below the 2:1 stoichiometric ratio of H_2S and SO_2 for the Claus reaction results in a loss of Claus efficiency. Figure 3-2 illustrates the variation of recovery efficiency with H_2S/SO_2 concentration ratio in the Claus converters.

Operation of a Claus plant below capacity may impair Claus efficiency somewhat. One vendor has reported a two or three percent loss in recovery when the Claus plant was turned down to 20 percent of design capacity.[16] Another vendor reports no loss in recovery efficiency when operating at two-thirds of capacity.[17]

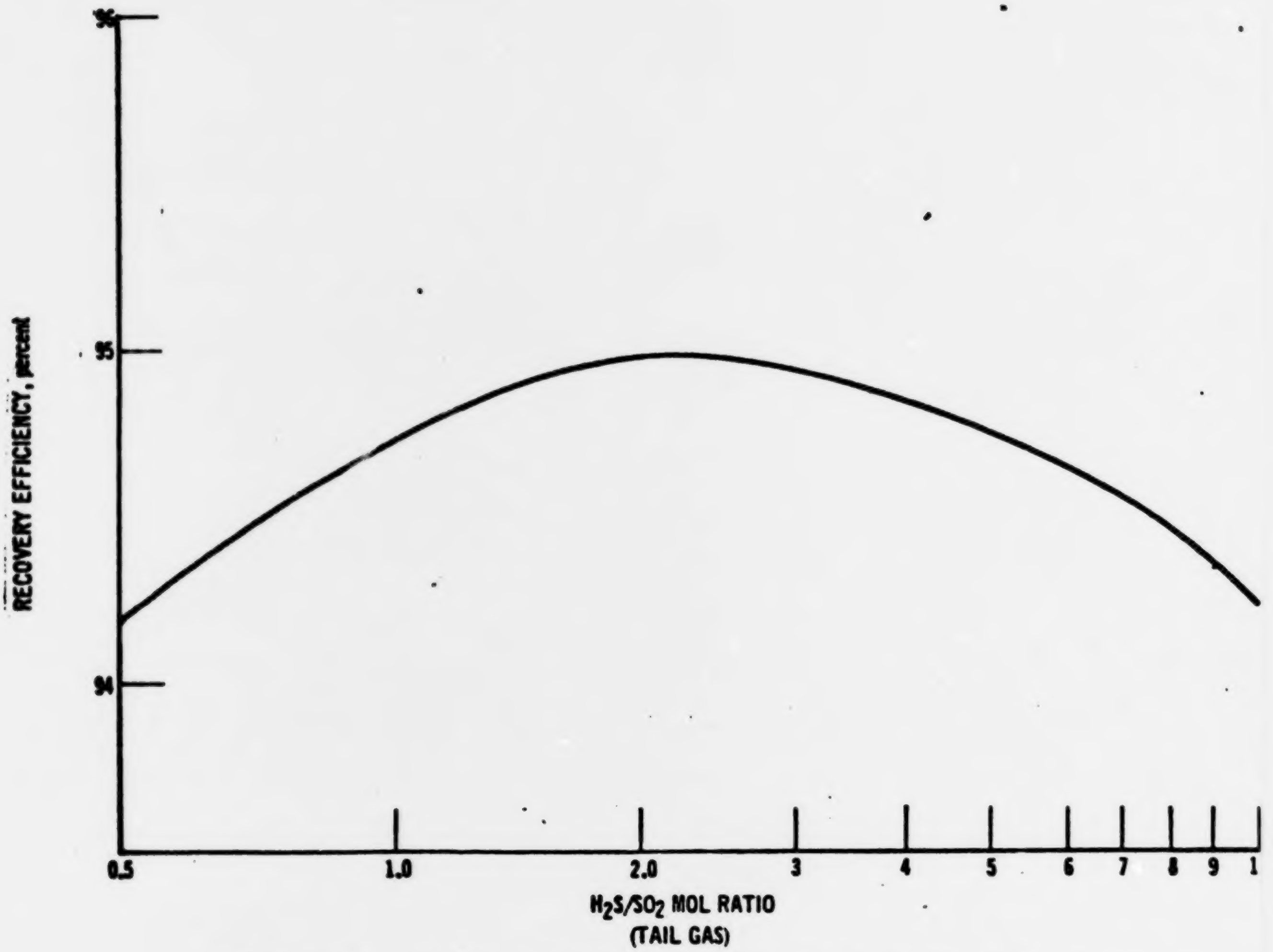

Figure 3-2. Theoretical Claus sulfur recovery efficiency vs. Mole Ratio.

Although the impact of process variables as discussed above represents in most cases a loss of only one to three percent efficiency, at the relatively high efficiencies typical of Claus operations (95%), a one to three percent efficiency loss represents a 20 to 60 percent increase in uncontrolled sulfur emissions.

The Stretford Process

The Stretford process[18] shown in Figure 3-3 is a one-step process to convert H_2S directly to elemental sulfur. At present the Stretford process is the only commercial sulfur recovery process which has supplanted conventional amine treating and Claus sulfur recovery in a refinery. Although the Stretford is installed in only one U.S. refinery, it has found application in several refineries as part of the tail gas cleanup process for Claus plants.

Refinery fuel gas or process gas is passed into a countercurrent column where the hydrogen sulfide in the gas is absorbed in the Stretford solution.

A summary of the Stretford reactions is as follows:

(a) Absorption of H_2S

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3$$

(b) Precipitation of sulfur

$$2NaVO_3 + NaHS + NaHCO_3 \rightarrow S\downarrow + Na_2V_2O_5 + Na_2CO_3 + H_2O$$

(c) Regeneration of sodium vanadate

$$Na_2V_2O_5 + \text{ADA* (oxidized)} \rightarrow 2NaVO_3 + \text{ADA (reduced)}$$

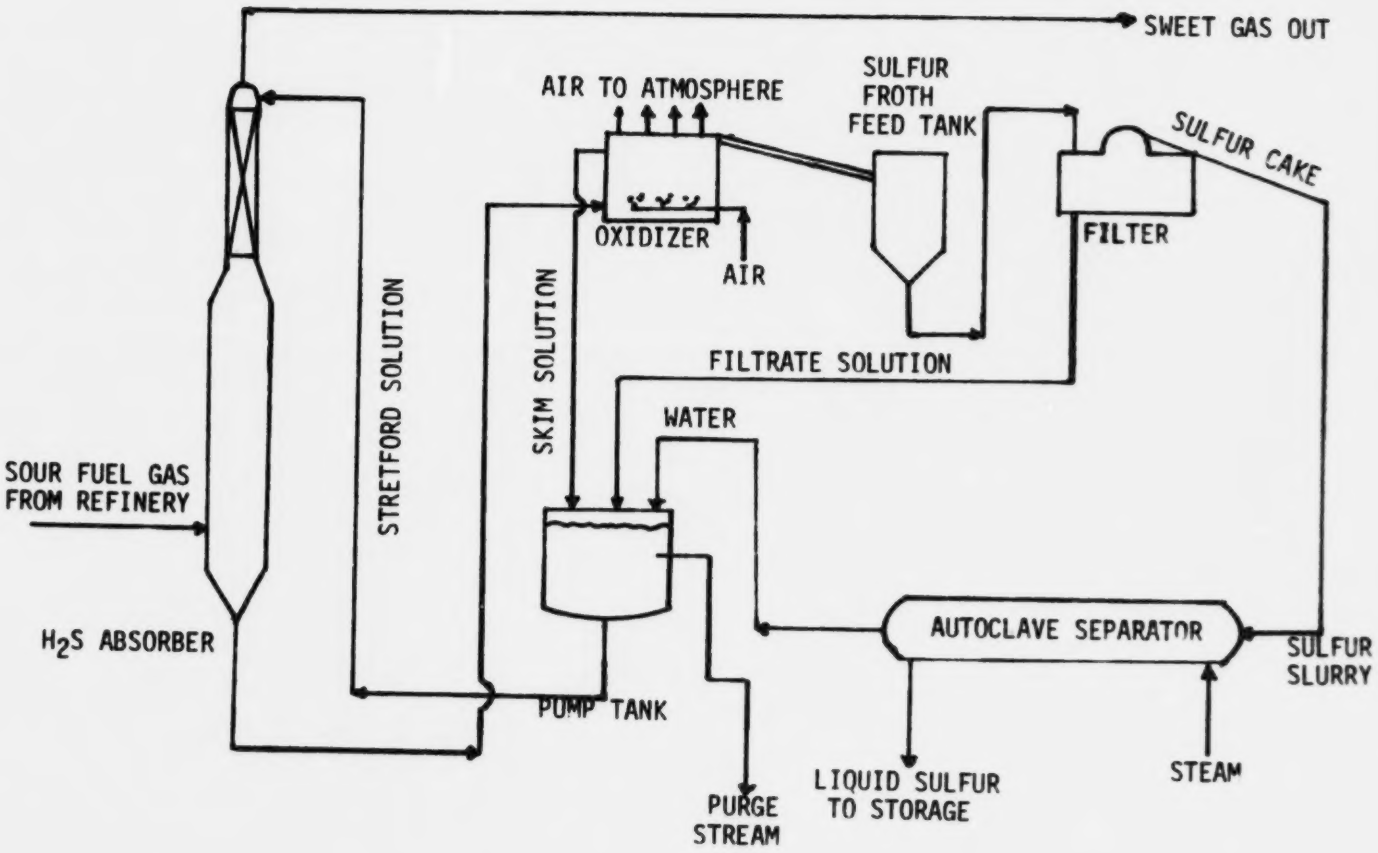
SWEET GAS OUT
AIR TO ATMOSPHERE
SULFUR FROTH FEED TANK
SULFUR CAKE
OXIDIZER
AIR
FILTER
STRETFORD SOLUTION
SKIM SOLUTION
FILTRATE SOLUTION
WATER
SOUR FUEL GAS FROM REFINERY
H_2S ABSORBER
AUTOCLAVE SEPARATOR
SULFUR SLURRY
PUMP TANK
PURGE STREAM
LIQUID SULFUR TO STORAGE
STEAM

Figure 3-3. Stretford process.

(d) Regeneration of ADA

ADA (reduced) + 1/2 O_2 (air) → ADA (oxidized)

(e) Overall reaction

$H_2S + 1/2\ O_2 \rightarrow S\downarrow + H_2O$

After recirculation through the H_2S absorber, the Stretford solution is retained in a holding tank to allow completion of sulfur precipitation. The Stretford solution is then regenerated by air blowing and reduced vanadium is restored by oxygen transfer from the ADA*

Sulfur formed in the solution is floated to the top of the oxidizer by air where the froths overflow to a settling tank. Sulfur settles as a sludge in the settling tank and is separated and recovered.

Some adverse side reactions occur due to increased liquor temperature and trace oxidizing gases contained in the fuel gas (notably oxygen, SO_2 and HCN) and result in the buildup of sodium thiosulfate and related compounds in the circulating liquor which must be purged from the system. The rate of thiosulfate formation depends on the partial pressure of the contaminant gas in the inlet gas stream and the pH and temperature of the liquor. Formation of thiosulfate is quite low, below about 100°F.

Purge stream rates range from 1.5 to 15 gallons per 100 moles of feed gas to the Stretford absorber.[19]

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*Anthraquinone Disulfonic Acid

The major advantage of the Stretford process is the overall reduction in emissions, both in the desulfurized fuel gas or process gas and the emissions from the sulfur recovery plant. Outlet sulfur loadings have been designed for less than 10 ppmv H_2S in the fuel gas or process gas.[20] COS and CS_2 are not recovered by the Stretford process; however, COS and CS_2 in fuel gases or process gases are much lower than the levels emitted from Claus plants. Essentially no sulfur is emitted from the oxidizer tank; hence, sulfur emissions from the Stretford sulfur recovery portion are nil. Emissions are relatively unaffected by process variables, although water wastes and chemical consumption are highly dependent upon operation.

The primary disadvantage of the Stretford process is the lack of operating experience in the U.S. In the one U.S. refinery application, the Stretford has yet to demonstrate good operability, experiencing numerous design and operating problems.[21] With time, however, the design and operational problems will undoubtedly be resolved so that the Stretford process will be competitive with the Claus process in refinery applications.

Other Alternative Processes

Other sulfur removal and recovery processes which could conceivably replace conventional amine treating and Claus sulfur recovery include the Giammarco-Vetrocoke H_2S Process and the Sulfox Process.[22,23] The Giammarco-Vetrocoke H_2S removal process is similar to the Stretford process, except that arsenate replaces vanadate in the scrubbing solution. The Sulfox process uses an aqueous ammonia solution to absorb H_2S. Elemental sulfur is produced by oxidizing the solution over a catalyst.

The Giammarco-Vetrocoke process has been applied to natural gas processing but has not yet been used in refinery sulfur recovery. The Sulfox process is designed specifically for refinery sulfur recovery but was only recently announced. Since neither process has any operating experience in refinery applications, a detailed discussion of operation and emissions is not included.

3.2 EXISTING EMISSION CONTROL REGULATIONS FOR SULFUR RECOVERY PLANTS

Table 3-2 summarizes current state emission control regulations for both existing and new sulfur recovery plants. The most stringent regulations for sulfur plant emissions are found in Florida, Los Angeles County, and Philadelphia. Florida regulations specify maximum allowable sulfur emissions as 0.004 lb SO_2 per lb sulfur input, or a 99.8 percent sulfur recovery (equivalent to ~500 ppmv total sulfur on an undiluted basis).[24] Los Angeles County restricts emissions to 500 ppmv sulfur calculated as SO_2 equivalent,[25] while Philadelphia restricts refinery sulfur plants to 500 ppmv SO_2.[26]

State codes applicable to sulfur recovery plants are generally expressed in pounds of sulfur input. A majority of states which have sulfur emission regulations for sulfur recovery plants have the same regulation, 0.01 lbs S/lb S input, or 99 percent sulfur recovery.[27]

The format of standards in Table 3-2 shows some states regulating SO_2 only, while several have standards for "sulfur emissions." The

Table 3-2

State Regulations for Sulfur Recovery Plants

State	Regulation	
	Existing Plants	New Plants
Alabama	0.16 lb S/lb S input	0.08 lb S/lb S input
Arkansas	ground level concentrations only	ground level concentrations only
Colorado	ground level concentrations only	ground level concentrations only
Connecticut	0.01 lb S/lb S input	0.01 lb S/lb S input
Delaware	2000 ppmv SO_2	2000 ppmv SO_2
Florida	0.004 lb SO_2/lb S input	0.004 lb SO_2/lb S input
Louisiana	0.01 lbs S/lb S input	0.01 lbs S/lb S input
New Hampshire	0.01 lbs S/lb S input	0.01 lbs S/lb S input
New Jersey	15,000 ppmv SO_2	15,000 ppmv SO_2
Ohio	0.01 lb S/lb S input	0.01 lb S/lb S input
Oklahoma	———	0.01 lb S/lb S input
Pennsylvania	(a)	(a)
Texas	(b)	2200 ppmv SO_2^{d} (Ref. 28)
Utah	———	(c)
Virginia	0.05 lb S/lb S input	0.05 lb S/lb S input
West Virginia	0.06 lb S/lb S input	0.06 lb S/lb S input

(a) According to $A=0.32\ E^{-0.5}$ where E = plant rating in LT/D and A = allowable emissions in lb SO_2/lb S input.

(b) 214 lbs SO_2/hr/1000 scfm effluent flow rate.

(c) 80% control for new sources with uncontrolled sulfur emissions $\geq$250 ton/year.

(d) at incinerator outlet, calculated for 50% excess air.

intent of sulfur emission codes is not specified, but assumed to be SO_2 regulation only, since emissions of H_2S or CS_2 at these levels would incur severe odor problems.

3.3 REFERENCES

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2. World Wide HPI Construction Boxscore, Hydrocarbon Processing, Section 2, February 1974, pp. 3-10.
3. Reference 1.
4. Reference 2.
5. Reference 1, page C-1.
6. Beavon, David K., and Vaell, Raoul P., "The Beavon Sulfur Removal Process for Purifying Claus Plant Tail Gas, presented at the 37th Midyear Meeting, API Division of Refining, May 8-11, 1972, p. 272.
7. Reference 1, p. 30.
8. Beers, W.D., "Characterization of Claus Plant Emissions," EPA Contract 68-02-0242, Task No. 2, April 1973, p. 9.
9. Letter, O.C. Roddy, Vice President, Ralph M. Parsons Co. to W.D. Beers, Processes Research Inc., March 23, 1972.
10. Letter, D.F. Cole, Contract Engineer, J.F. Pritchard & Co. to W.D. Beers, Processes Research Inc., March 23, 1972.
11. Reference 8, p. 9.
12. Grekel, H. et al., "Why Recover Sulfur from H_2S?" Oil and Gas Journal, Oct. 28, 1968, p. 95.
13. Reference 12.
14. Reference 10.
15. Reference 9.
16. Reference 9.
17. Reference 10.
18. Reference 1, pp. 32-35.

19. Reference 1, p. 36.

20. Brochure, "Sulfur Recovery Qualifications and Experience," J.F. Pritchard and Company, Kansas City, Mo., Sept. 1973, p. A-4.

21. Letter, L.W. Larsen, Sun Oil Company to James F. Durham, ESED, OAQPS, EPA, dated January 2, 1975.

22. Reference 1, pp. 38-40.

23. Conser, R.C., "Here's a New Way to Clean Process Gases," Oil and Gas Journal, April 1, 1974, pp. 67-70.

24. Duncan, L.J., "Analysis of Final State Implementation Plans - Rules and Regulations," EPA Contract 68-02-0248, July 1972, (APTD-1334) pp. 55-57.

25. "Rules and Regulations," County of Los Angeles Air Pollution Control District, Rule 53.2.

26. Section II (B), Air Management Regulation III of the Air Pollution Control Board, City of Philadelphia, adopted April 10, 1970.

27. Reference 24, p. 12.

28. Private communication, Frank J. Spuhler, Texas Air Control Board to Charles B. Sedman, Industrial Studies Branch, ESED, OAP, January 17, 1974.

4. EMISSION CONTROL TECHNOLOGY

4.1 ALTERNATIVE EMISSION CONTROL TECHNIQUES

Removal of sulfur compounds from Claus plant tail gas is possible by three general schemes:

(1) Extension of the Claus reaction to increase overall sulfur recovery;

(2) Conversion of sulfur gases to sulfur dioxide (SO_2) followed by SO_2 removal technology;

(3) Conversion of sulfur gases to hydrogen sulfide (H_2S) followed by H_2S removal technology.

Option (1) is conceptually simple and requires only adjustments in the operating temperature of the three-stage conventional Claus.

Option (2) is attractive because the SO_2 removed can be recycled to the Claus plant. An incinerator which is standard equipment for sulfur plants oxidizes all gaseous sulfur compounds to SO_2 prior to scrubbing.

Option (3) is attractive because H_2S removal technology is advanced and H_2S can be recycled to the Claus plant or directly oxidized to sulfur. Conversion of all sulfur species to H_2S requires heat, a reducing gas, and a reducing catalyst.

Figure 4-1 shows the various commercially available control schemes and how each utilizes options (1), (2), and (3) to remove sulfur from Claus tail gas. Although the literature cites many tail gas control systems, those described below were chosen as representing available control technology for Claus sulfur plants and are presently in commercial operation.

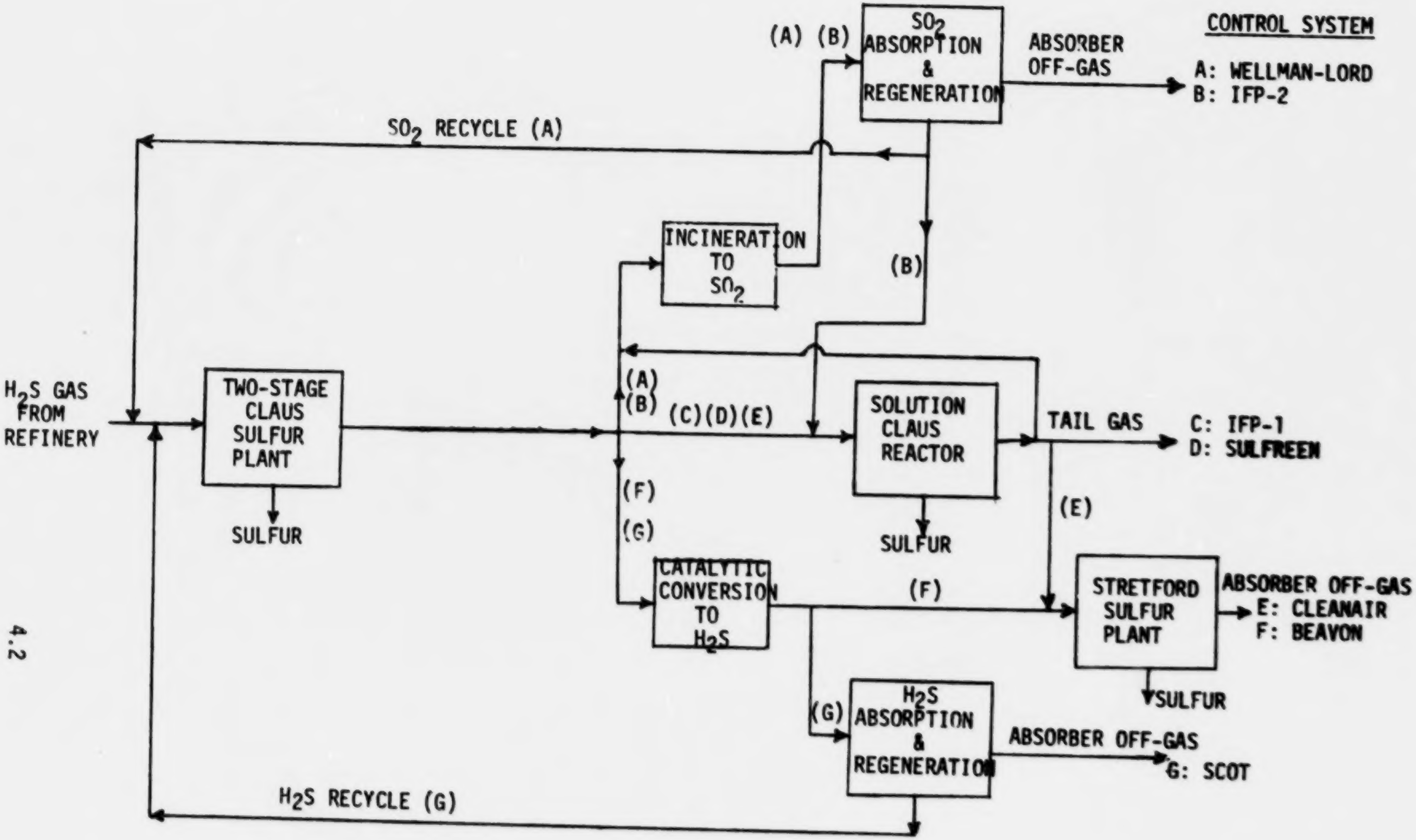

CONTROL SYSTEM
A: WELLMAN-LORD
B: IFP-2
C: IFP-1
D: SULFREEN
E: CLEANAIR
F: BEAVON
G: SCOT
H_2S GAS FROM REFINERY
TWO-STAGE CLAUS SULFUR PLANT
SULFUR
SO_2 RECYCLE (A)
(A) (B)
SO_2 ABSORPTION & REGENERATION
ABSORBER OFF-GAS
INCINERATION TO SO_2
(B)
(A)
(B)
(C)(D)(E)
SOLUTION CLAUS REACTOR
SULFUR
TAIL GAS
(E)
(F)
(G)
CATALYTIC CONVERSION TO H_2S
(F)
STRETFORD SULFUR PLANT
ABSORBER OFF-GAS
SULFUR
(G)
H_2S ABSORPTION & REGENERATION
ABSORBER OFF-GAS
H_2S RECYCLE (G)

Figure 4-1. Emission control systems for refinery Claus plants.

Extension of the Claus Reaction

The conventional Claus plant, having two or three stages, was discussed in Chapter 3. Such a unit has a recovery efficiency of about 95%. To gain further improvement in sulfur recovery efficiency via the Claus reaction, the temperature can be lowered to shift the equilibrium of the Claus reaction toward formation of additional sulfur. Two processes have been developed for reducing emissions through extension of the Claus reaction by operation at low temperatures. These are the IFP-1 and Sulfreen processes.

IFP-1 PROCESS[1,2]

The basic reaction involved in the IFP-1 process (Figure 4-2) is the same one which takes place in the reactors of a Claus unit:

$$2H_2S + SO_2 \overset{\text{Catalyst}}{\rightleftarrows} 3S\downarrow + 2H_2O$$

Tail gas which exits a Claus unit at 265-285°F can be fed directly into the IFP reactor without cooling the gas. The reactor is a packed column with a specially designed "boot" for collecting sulfur. Metal salts catalyze the reaction which takes place in a high boiling polyglycol (PEG) solvent above the melting point of sulfur--generally in the range of 250-260°F. The metal salts form a complex with H_2S and SO_2 in the feed gas, which in turn reacts with additional H_2S and SO_2 to form elemental sulfur and regenerate the catalyst complex. Sulfur coalesces and settles into the boot of the reactor, from which it is drawn as a molten product.

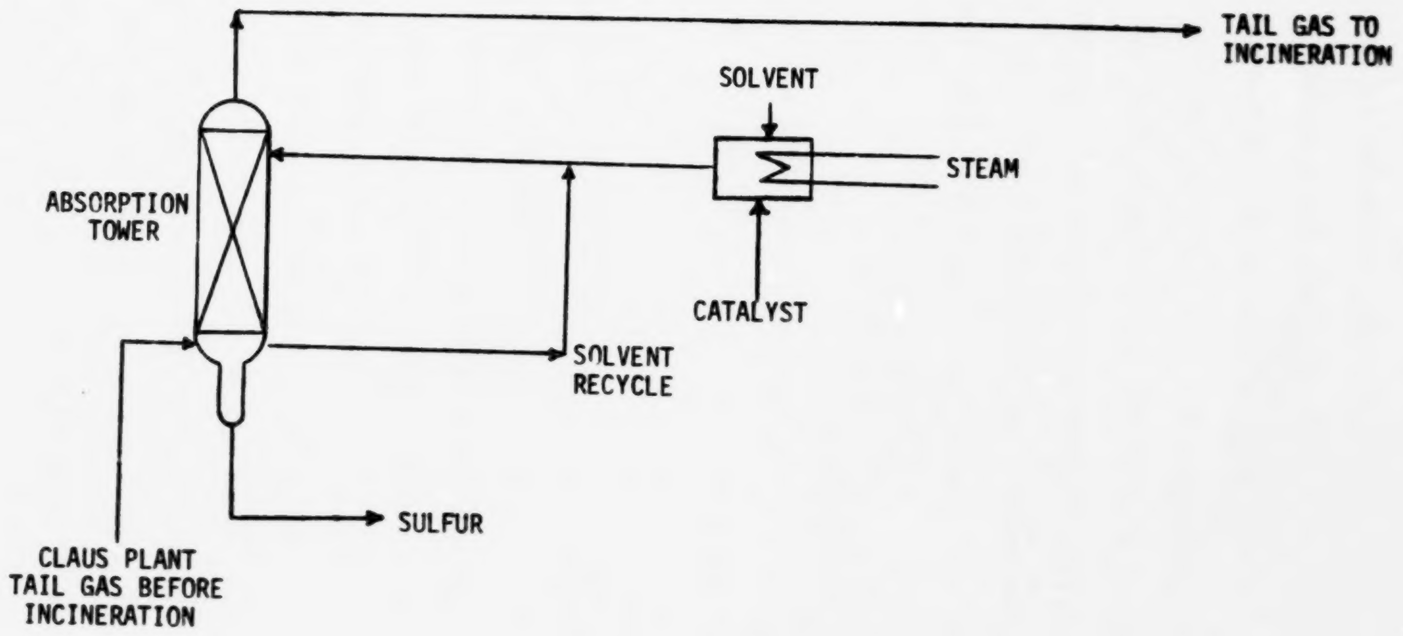

TAIL GAS TO INCINERATION
SOLVENT
STEAM
ABSORPTION TOWER
CATALYST
SOLVENT RECYCLE
SULFUR
CLAUS PLANT TAIL GAS BEFORE INCINERATION

Figure 4-2. Flow diagram for IFP-1 Claus tail-gas clean-up process.

The gas leaving the reactor contains about 850 ppm H_2S and 420 ppm SO_2, assuming a 90 percent conversion. Conversion efficiency is maximized at the 2:1 stoichiometric H_2S/SO_2 ratio required by the Claus reaction. Above or below this ratio the conversion efficiency diminishes; hence, process controls must effectively keep the H_2S/SO_2 ratio in the IFP reactor feed as near 2:1 as possible. Also, below 2:1 H_2S/SO_2 ratio in the gas stream, the solvent tends to evolve absorbed H_2S, which also increases ultimate sulfur emissions.

Besides H_2S and SO_2, about 300 ppm sulfur vapor is evolved with the exit gas. This is roughly the equilibrium concentration of sulfur in the vapor phase at 260°F. COS and CS_2 formed in the Claus plant are not affected by the IFP-1; hence, they exit at approximately the same concentrations as in the feed gas. The reactor exhaust containing 1500-2500 ppm sulfur and some entrained solvent is incinerated before discharge to the atmosphere.

SULFREEN PROCESS[3,4]

The Sulfreen process (Figure 4-3) reduces the sulfur content in Claus plant tail gas by further promoting the Claus reaction on a catalytic surface in a gas/solid batch reactor. Claus tail gas is first scrubbed with liquid to wash out entrained sulfur liquid and sulfur vapor. The tail gas is then introduced to a battery of reactors where the Claus reactions are carried out at lower temperatures (260-300°F) than those utilized in the sulfur plant. Lower temperatures push the Claus reaction toward completion due to favorable equilibrium conditions. The catalyst is usually activated carbon, though alumina is also used.

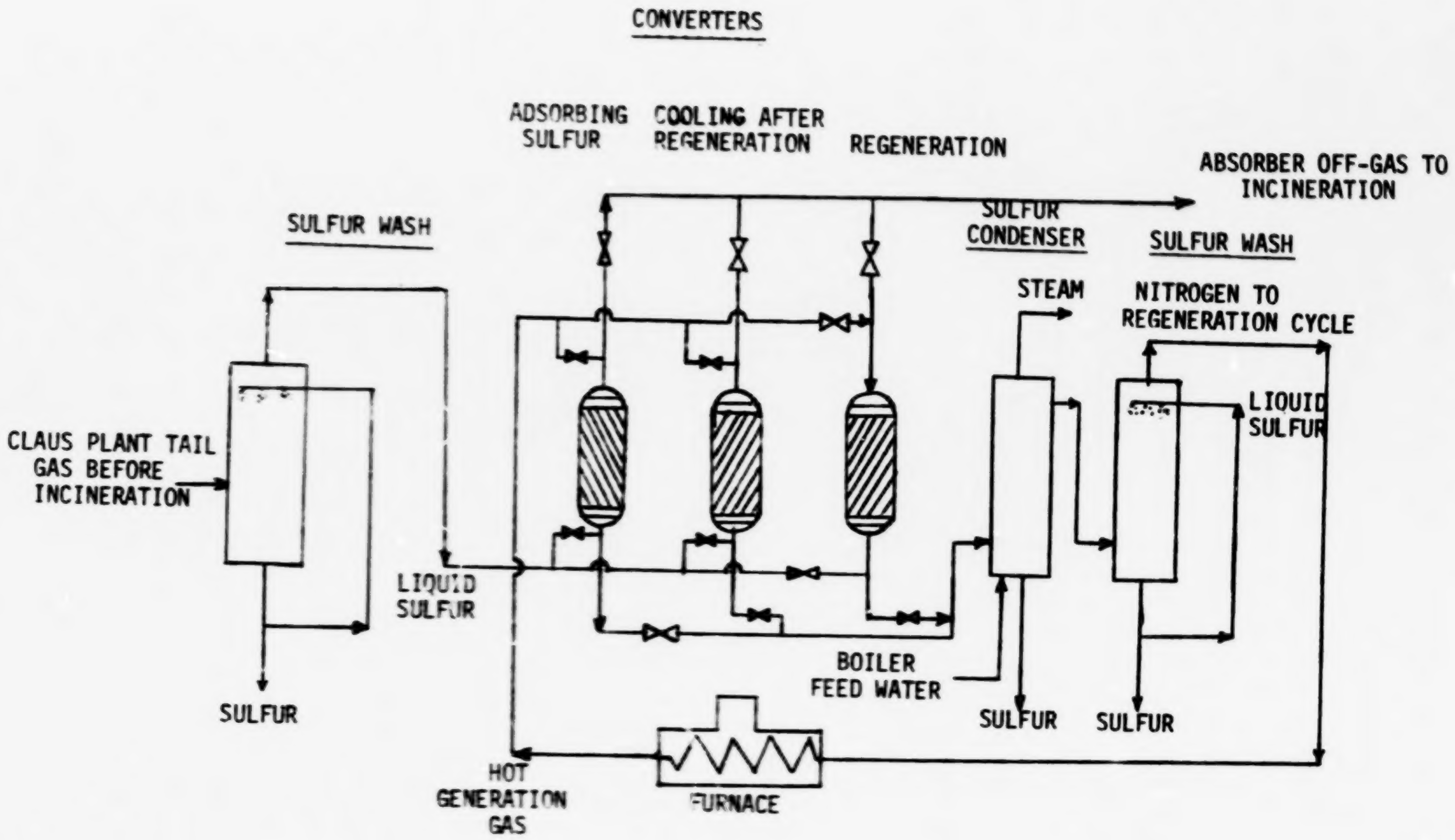

CONVERTERS
ADSORBING SULFUR
COOLING AFTER REGENERATION
REGENERATION
ABSORBER OFF-GAS TO INCINERATION
SULFUR WASH
SULFUR CONDENSER
SULFUR WASH
STEAM
NITROGEN TO REGENERATION CYCLE
CLAUS PLANT TAIL GAS BEFORE INCINERATION
LIQUID SULFUR
LIQUID SULFUR
BOILER FEED WATER
SULFUR
SULFUR
SULFUR
HOT GENERATION GAS
FURNACE

Figure 4-3. Flow diagram for the Sulfreen process.

A regeneration gas, essentially nitrogen, periodically desorbs the sulfur-laden catalyst beds. Nitrogen is heated and cycles through the catalyst bed at approximately 570°F until all water and CO_2 are driven off.

For the desorption of sulfur, the temperature is raised to 750°F where sulfur vaporizes, is swept away with the nitrogen, and precipitates in a condenser. The carrier gas is further scrubbed in a sulfur wash before returning to the regeneration cycle.

The process reduces entrained sulfur, since the catalyst acts as an absorbent for liquid sulfur. However, tail gas passing through the catalyst bed retains several hundred ppm sulfur vapor in equilibrium with liquid sulfur. H_2S and SO_2 are reduced by 80-85 percent to levels of about 1800 ppmv H_2S and 900 ppm SO_2. As with the IFP-1 process, the levels of H_2S and SO_2 are highly dependent upon maintaining the 2:1 ratio of H_2S/SO_2 in the Claus tail gas. COS and CS_2 are not affected by the Sulfreen process.

A Sulfreen unit may consist of as little as three reactors, two in absorption and one in desorption service. The gases from the reactors in desorption service are incinerated before discharge to the atmosphere.

Conversion to SO_2 Followed by SO_2 Recovery

Two processes have been developed to reduce emissions from Claus sulfur plants through conversion of the sulfur compounds present in the sulfur plant tail gas to SO_2, followed by recovery of the SO_2. These are the Wellman-Lord and IFP-2 processes. Incineration of the sulfur plant tail gas effectively converts all the sulfur compounds present to SO_2 and this is recovered in a conventional SO_2 scrubbing system. In both processes the SO_2 recovered is recycled to the sulfur plant for eventual conversion to elemental sulfur by the Claus reaction.

WELLMAN-LORD PROCESS[5,6]

The Wellman-Lord process (Figure 4-4) uses a wet regenerative system to reduce the stack gas sulfur concentration to less than 250 ppmv. Sulfur constituents in Claus plant tail gases are oxidized to SO_2 in the standard sulfur plant incinerator, then cooled and quenched to reduce the gas temperature and remove excess water. The SO_2 rich gas is then contacted countercurrently with a sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$) solution which absorbs SO_2 to form additional bisulfite. The principal reaction between SO_2 and the absorbent solution is:

$$SO_2 + Na_2SO_3 + H_2O \rightleftarrows 2NaHSO_3$$

The absorber off-gas is reheated and vented to the atmosphere at less than 250 ppmv SO_2 and negligible amounts of other sulfur compounds. Any SO_3 produced by the incineration is preferentially absorbed.

SO_2-rich solution is boiled in an evaporator-crystallizer, wherein the bisulfite solution decomposes to SO_2 and H_2O vapor and sodium sulfite is precipitated according to the reaction:

$$2NaHSO_3 \overset{heat}{\rightleftarrows} Na_2SO_3\downarrow H_2O + SO_2\uparrow$$

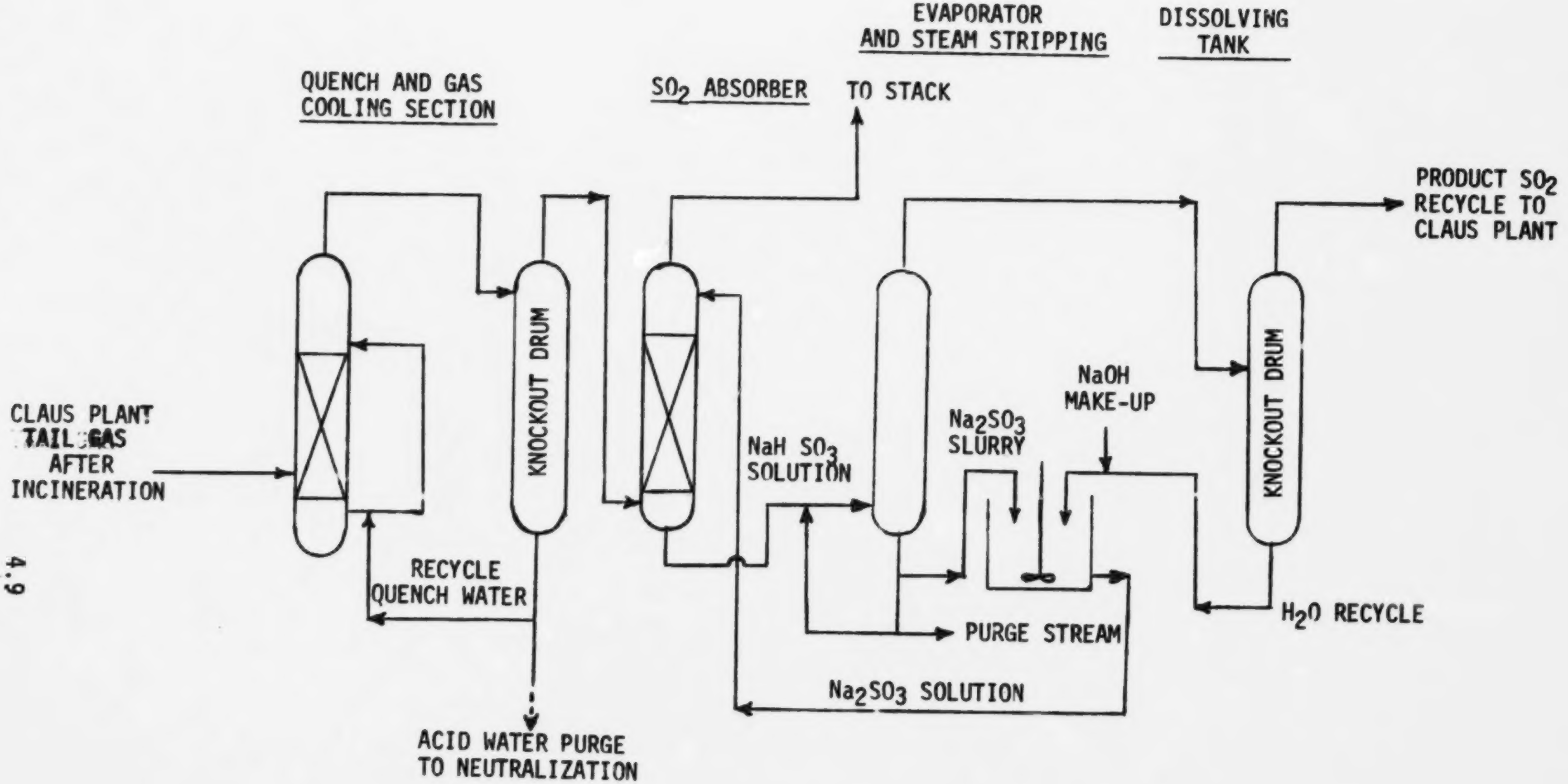

QUENCH AND GAS COOLING SECTION
SO_2 ABSORBER
TO STACK
EVAPORATOR AND STEAM STRIPPING
DISSOLVING TANK
PRODUCT SO_2 RECYCLE TO CLAUS PLANT
CLAUS PLANT TAIL GAS AFTER INCINERATION
KNOCKOUT DRUM
NaH SO_3 SOLUTION
Na_2SO_3 SLURRY
NaOH MAKE-UP
KNOCKOUT DRUM
RECYCLE QUENCH WATER
PURGE STREAM
H_2O RECYCLE
Na_2SO_3 SOLUTION
ACID WATER PURGE TO NEUTRALIZATION

Figure 4-4. Flow diagram for the Wellman-Lord SO_2 recovery process.

Sulfite crystals are separated and redissolved for reuse as lean solution to the absorber.

The wet SO_2 gas flows to a partial condenser where most of the water is condensed and reused to dissolve the sulfite crystals. The enriched SO_2 stream is then recycled back to the Claus plant for conversion to elemental sulfur.

IFP-2 PROCESS[7,8]

With the IFP-2 process (Figure 4-5), Claus plant tail gas is incinerated to convert all sulfur species to SO_2. The incinerated gas is cooled and then fed to an ammonia scrubber, where SO_2 is absorbed and converted to ammonium sulfite and ammonium bisulfite by the following reactions:

$$2NH_4OH + SO_2 \rightleftharpoons H_2O + (NH_4)_2SO_3$$

$$NH_4OH + SO_2 \rightleftharpoons NH_4HSO_3$$

Sulfates and thiosulfates are also formed in the ammonia scrubber by the following side reactions:

$$2NH_4OH + SO_2 + 1/2O_2 \rightarrow H_2O + (NH_4)_2SO_4$$

$$2NH_4OH + SO_3 \rightarrow (NH_4)_2SO_4 + H_2O$$

$$2NH_4OH + SO_2 + S \rightarrow H_2O + (NH_4)_2S_2O_3$$

Gas leaving the absorber is reheated and vented to the atmosphere at less than 250 ppm SO_2 concentration.

The SO_2 rich solution is fed to an SO_2 regenerator where the sulfite and bisulfite are thermally decomposed to SO_2, NH_3, and H_2O. A saturated solution containing ammonium sulfate and thiosulfate is drawn from the bottom of the SO_2 regenerator and fed to a sulfate reducer.

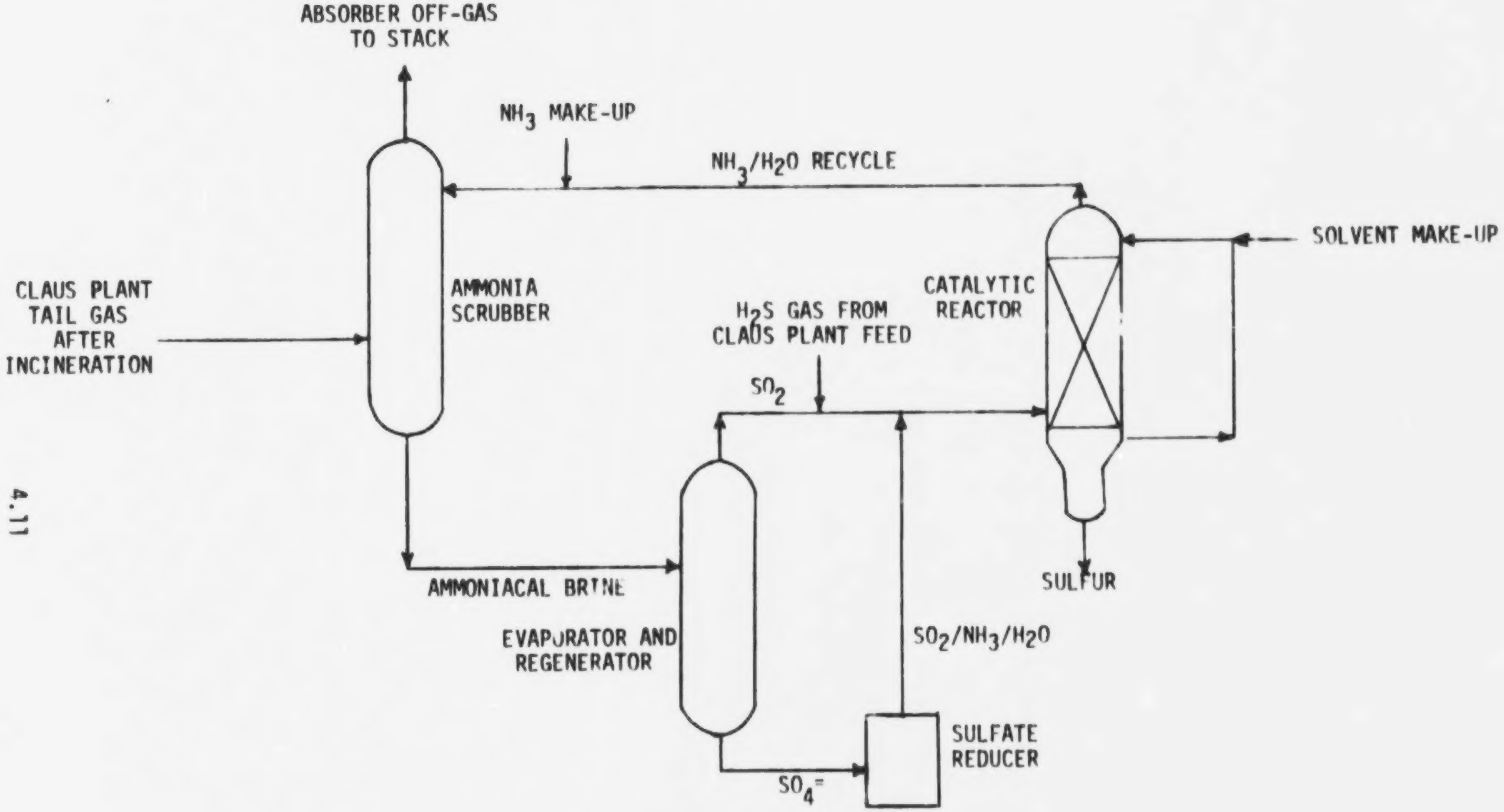

ABSORBER OFF-GAS TO STACK
NH_3 MAKE-UP
NH_3/H_2O RECYCLE
SOLVENT MAKE-UP
CLAUS PLANT TAIL GAS AFTER INCINERATION
AMMONIA SCRUBBER
CATALYTIC REACTOR
H_2S GAS FROM CLAUS PLANT FEED
SO_2
AMMONIACAL BRINE
SULFUR
EVAPORATOR AND REGENERATOR
$SO_2/NH_3/H_2O$
SULFATE REDUCER
$SO_4^=$

Figure 4-5. Flow diagram for IFP-2 Claus tail-gas clean-up process.

In the sulfate reducer, the sulfates and thiosulfates formed in the side reactions are thermally decomposed per the following reactions:

$$(NH_4)_2SO_4 \rightarrow NH_4HSO_4 + NH_3\uparrow$$

$$(NH4)_2S_2O_3 \rightarrow 2NH_3\uparrow + SO_2\uparrow + S + H_2O\uparrow$$

$$2NH_4HSO_4 + S \rightarrow 3SO_2\uparrow + 2NH_3\uparrow + 2H_2O\uparrow$$

Gases from the SO_2 regenerator and sulfate reducer are combined with an H_2S rich stream (normally Claus plant feed gas) and fed to a catalytic reactor where they are contacted with a polyethylene glycol solvent. The H_2S and SO_2 react in the solution to form elemental sulfur. Sulfur is withdrawn in the molten state and sent to the Claus plant sulfur pit.

Gases from the reactor are cooled to condense out water and NH_3 as NH_4OH. The NH_4OH solution is returned to the ammonia scrubber. Any H_2S or SO_2 which leaves the reactor and is not absorbed by the NH_4OH solution is recycled to the incinerator and from there to the ammonia scrubber.

Conversion to H_2S Followed by H_2S Recovery

Three processes have been developed to reduce emissions from Claus sulfur plants through conversion of the sulfur compounds present in the sulfur plant tail gas to H_2S, followed by H_2S recovery. These are the Beavon, Cleanair and SCOT processes. In each of these processes, the sulfur plant tail gas is mixed with a reducing gas such as hydrogen and passed over a reducing catalyst. Most of the sulfur compounds present are converted to H_2S. Both the Beavon and Clean air processes then use the Stretford process (discussed in Chapter 3) to absorb the H_2S and convert it directly to elemental sulfur. In the SCOT process the H_2S is absorbed in a conventional H_2S scrubbing system and then recycled to the Claus sulfur plant for eventual conversion to elemental sulfur.

BEAVON PROCESS[9,10]

The Beavon process (Figure 4-6) begins by converting sulfur present in the tail gas (SO_2, COS, CS_2, and elemental sulfur) back to H_2S. This is done by hydrogenation and hydrolysis under moderate conditions of temperature and pressure similar to those in the Claus plant. Before the tail gas enters the packed bed hydrogenation reactor, fuel gas is combusted substoichiometrically in an inline burner to produce the reducing conditions necessary to convert sulfur gases to H_2S. The combustion products are mixed with the tail gas to provide a reducing atmosphere. Extra hydrogen may be made in the fuel-rich combustion chamber as required to supplement hydrogen already in the tail gas by the reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

A cobalt-molybdenum catalyst promotes the hydrogenation and hydrolysis reactions which reduce SO_2 to very low values and ($COS + CS_2$) to less than 100 ppmv. Elemental sulfur is completely reduced to H_2S. The reactions are:

$$S_8 + 8H_2 \rightarrow 8H_2S$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

$$COS + H_2O \rightleftharpoons CO_2 + H_2S$$

$$CS_2 + H_2O \rightleftharpoons H_2S + COS$$

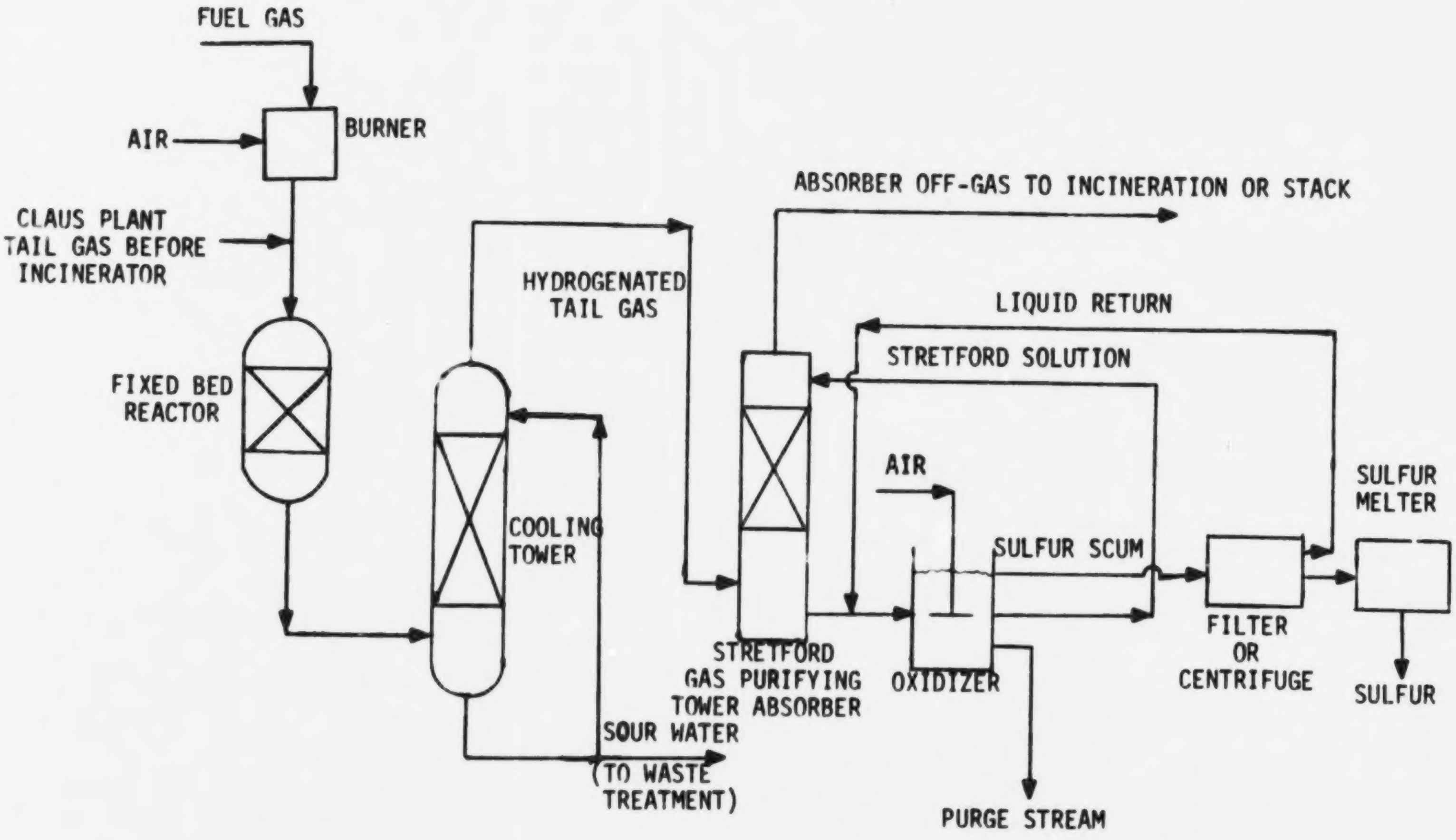

FUEL GAS
AIR
BURNER
CLAUS PLANT TAIL GAS BEFORE INCINERATOR
FIXED BED REACTOR
HYDROGENATED TAIL GAS
COOLING TOWER
SOUR WATER (TO WASTE TREATMENT)
ABSORBER OFF-GAS TO INCINERATION OR STACK
LIQUID RETURN
STRETFORD SOLUTION
STRETFORD GAS PURIFYING TOWER ABSORBER
AIR
SULFUR SCUM
OXIDIZER
PURGE STREAM
FILTER OR CENTRIFUGE
SULFUR MELTER
SULFUR

Figure 4-6. Flow diagram for the Beavon sulfur removal process.

$CS_2 + 2H_2S \rightleftharpoons CH_4 + 4S$

$4H_2 + CS_2 \rightleftharpoons 2H_2S + CH_4$

$COS + 4H_2 \rightleftharpoons H_2O + H_2S + CH_4$

After hydrogenation, the tail gas is cooled and water is removed. The H_2S-rich tail gas is fed to the Stretford circuit for removal of H_2S to less than 10 ppm. Final incineration before discharge to the atmosphere is optional.

CLEANAIR PROCESS[11,12]

The Cleanair process includes the Stretford process and two confidential processes. Figure 4-7 is a process diagram. An optional part of the Cleanair package includes a modification of the Claus plant first stage to include a reducing and hydrolysis catalyst. This causes the conversion of COS and CS_2 to H_2S according to the following reaction:

$COS + H_2O \rightleftharpoons H_2S + CO_2$

$CS_2 + 2H_2O \rightleftharpoons 2H_2S + CO_2$

Carbon dioxide also is decomposed to CO to prevent the recurrence of COS.

Claus tail gas, with essentially all gaseous sulfur as sulfur vapor, H_2S and SO_2, is quenched to reduce temperature and remove water and entrained sulfur. The cooled gas is fed into a reactor where H_2S and SO_2 (in a 2:1 ratio) react, lowering SO_2 to less than 250 ppmv. Both water and sulfur (products of the Claus reaction) are removed.

Next, the tail gas is sent to a Stretford unit where remaining H_2S is removed and oxidized to elemental sulfur. Residual SO_2,

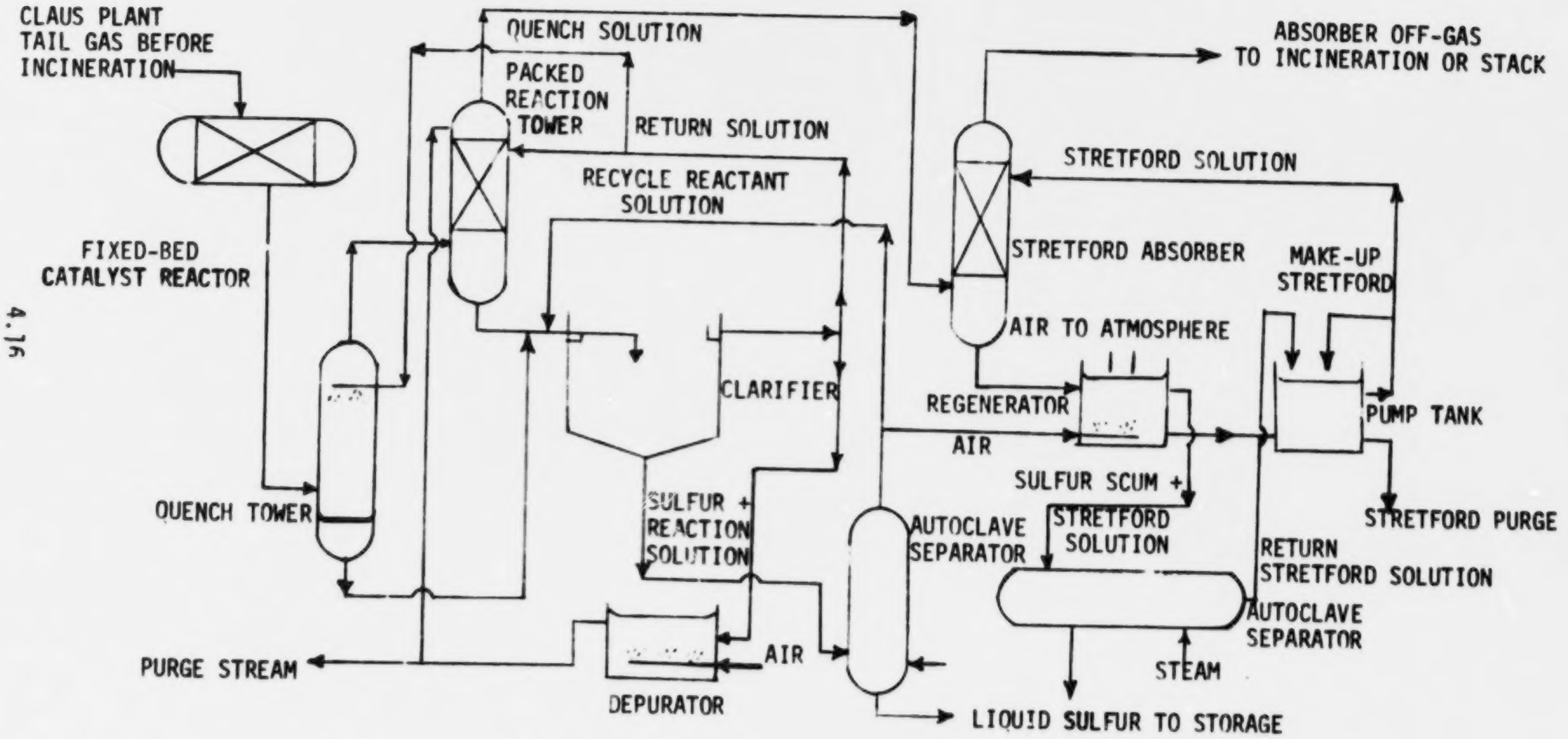

CLAUS PLANT
TAIL GAS BEFORE
INCINERATION
FIXED-BED
CATALYST REACTOR
QUENCH TOWER
PURGE STREAM
QUENCH SOLUTION
PACKED
REACTION
TOWER
RETURN SOLUTION
RECYCLE REACTANT
SOLUTION
CLARIFIER
SULFUR +
REACTION
SOLUTION
DEPURATOR
AIR
AUTOCLAVE
SEPARATOR
LIQUID SULFUR TO STORAGE
ABSORBER OFF-GAS
TO INCINERATION OR STACK
STRETFORD SOLUTION
STRETFORD ABSORBER
AIR TO ATMOSPHERE
REGENERATOR
AIR
SULFUR SCUM +
STRETFORD
SOLUTION
MAKE-UP
STRETFORD
PUMP TANK
STRETFORD PURGE
RETURN
STRETFORD SOLUTION
AUTOCLAVE
SEPARATOR
STEAM

Figure 4-7. Flow diagram for the Cleanair Claus tail-gas treatment process.

although absorbed by the Stretford solution, decomposes the solution and therefore increases chemical consumption and liquid purge rate. Residual COS and CS_2 will pass through unaffected. Purified gas may then be sent to an incinerator to oxidize residual sulfur to SO_2 (guaranteed less than 250 ppmv) and CO to CO_2 before discharge to the atmosphere.

SHELL CLAUS OFF-GAS TREATING (SCOT) PROCESS[13,14]

Similar to the Beavon process, the SCOT process (Figure 4-8) first converts all sulfur compounds and free sulfur in the tail gas to H_2S. Hydrogen, or hydrogen and carbon monoxide mixtures are used as the reducing gases while a cobalt/molybdenum-on-alumina catalyst promotes the reactions:

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

$$S_8 + 8H_2 \rightarrow 8H_2S$$

COS and CS_2 are reduced in reactions identical with those in the Beavon catalytic reactor. Where carbon monoxide is also present as a reducing agent, the following additional reactions may occur:

$$SO_2 + 3CO \rightarrow COS + 2CO_2$$

$$S_8 + 8CO \rightarrow 8COS$$

$$COS + H_2O \rightleftarrows CO_2 + H_2S$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

$$CO + H_2S \rightleftarrows COS + H_2$$

From the SCOT reactor, the tail gas containing less than 100 ppm ($COS + CS_2$) and 10 ppm SO_2 is cooled and excess water removed. The H_2S (at 20,000-40,000 ppmv) and some CO_2 are then removed by treating

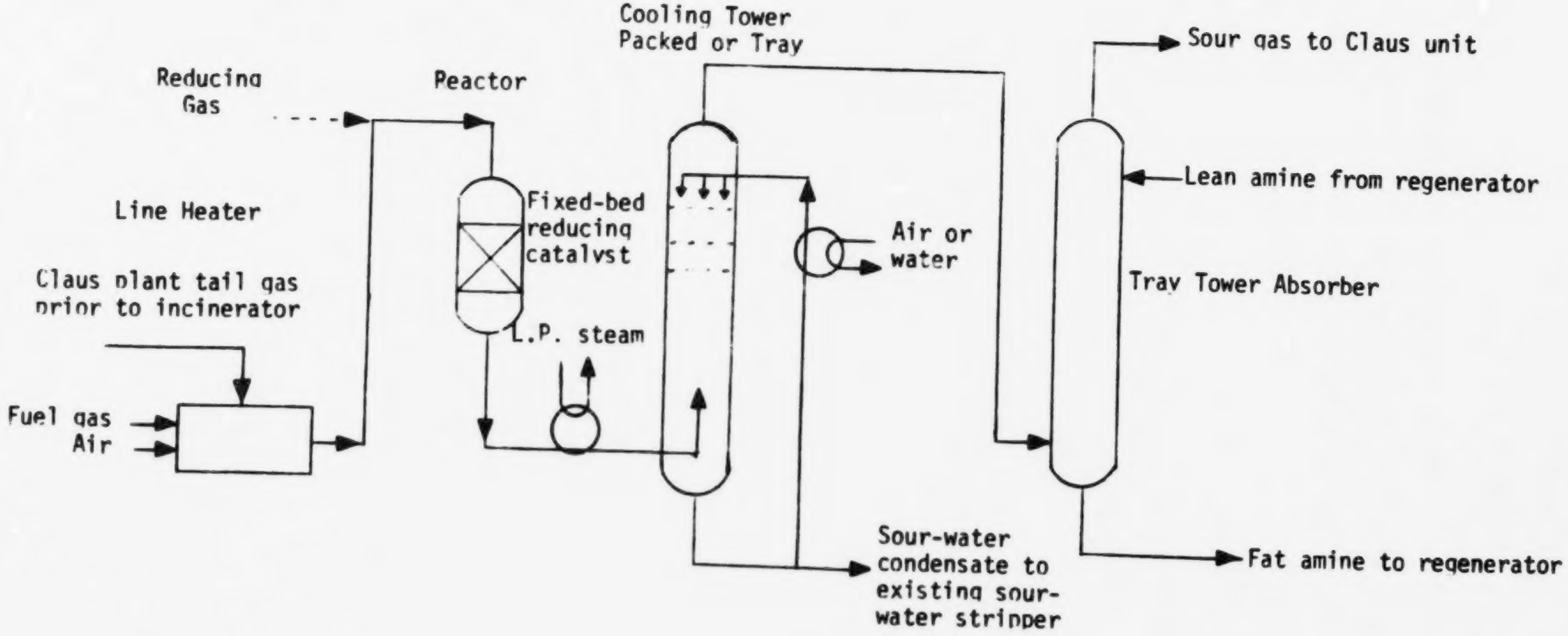

Reducing
Gas
Line Heater
Claus plant tail gas
prior to incinerator
Fuel gas
Air
Reactor
Fixed-bed
reducing
catalyst
L.P. steam
Cooling Tower
Packed or Tray
Air or
water
Sour-water
condensate to
existing sour-
water stripper
Sour gas to Claus unit
Lean amine from regenerator
Tray Tower Absorber
Fat amine to regenerator

Figure 4-8. FLOW DIAGRAM FOR THE SHELL CLAUS OFF-GAS TREATING PROCESS

with di-isopropanolamine solution in an absorption column. The H_2S-rich solution is regenerated by stripping H_2S in a conventional steam stripping column. Regenerator off-gas, mainly H_2S and some CO_2 is recycled as feed to the first stage of the Claus unit. The absorber off-gas, containing less than 300 ppmv H_2S is incinerated in a standard Claus incinerator.

4.2 COMMERCIAL STATUS OF TAIL GAS TECHNOLOGY

The Wellman-Lord process has demonstrated the longest trouble-free operation--over two years on a Claus plant.[15] Wellman-Lord units on Claus plants are in operation at three refineries with five additional units scheduled for start-up in 1974 and early 1975.[16] The IFP-2 process is being installed in three Japanese refineries.[17]

Of units designed specifically for Claus tail gas treating, the Beavon, SCOT, and IFP-1 units have been successfully operated in refineries. Four Beavon units have been running continuously at two refineries since July 1973.[18] Three other Beavon units started up during 1973, with three more scheduled for completion in 1974.[19] Two small SCOT units were installed in June 1973, and are currently in operation following some modifications.[20] At least seven more SCOT's were scheduled for start-up in 1974.[21]

The IFP-1 and Sulfreen processes have been applied to natural gas plants in France and Canada for about five years.[22] Also, the IFP-1 is currently in operation on six refinery sulfur plants in Japan and two in the U.S. with several more announced.[23]

The Cleanair process was installed at three U.S. refineries in 1973; but all are still awaiting start-up after process modifications.[24]

A detailed list of present and planned Claus tail gas control systems is presented in Table 4-1.

Table 4-1. LISTING OF ANNOUNCED TAIL GAS TREATING UNITS FCR CLAUS SULFUR PLANTS AS OF 3/1/74

Type Unit	Company/Location	Onstream Date	No. of Units	Number/Capacity Claus Plant, LT
Beavon	Union Oil Company/ Wilmington, California	July 1973	2	2/100
Beavon	Mobil Oil Company/ Torrance, California	July 1973	2	3/100
Beavon	Atlantic-Richfield/ Philadelphia, Pennsylvania	September 1973	1	1/140
Beavon	Getty Oil Company/ Delaware City, Delaware	November 1973	1	1/300
Beavon	Kobe Steel Co./Japan	October 1973	1	1/220
Beavon	Texaco, Inc./ Long Beach, California	March 1974	1	--
Beavon	Unknown/ Carribbean	April 1974	2	--
Beavon	Union Oil Co./ Rodeo, California	November 1974	3	--
Cleanair	Atlantic Richfield Corp. (ARCO)/ Wilmington, California	--	1	3/90
Cleanair	Gulf Oil Co./ Philadelphia, Pennsylvania	--	1	1/46
Cleanair	Santa Fe Springs Refinery (Gulf Oil Co.)/Santa Fe Springs, California	--	1	1/27
Cleanair	Techmashimport, U.S.S.R.	--	2	--
Wellman-Lord	Standard Oil of California/ Richmond, California	January 1975	1	1/290
Wellman-Lord	Kashima Oil Co./ Kashima, Japan	February 1974	1	1/180

Table 4-1. (Cont.) LISTING OF ANNOUNCED TAIL GAS TREATING UNITS FOR CLAUS SULFUR PLANTS AS OF 3/1/74

Type Unit	Company/Location	Onstream Date	No. of Units	Number/Capacity of Claus Plant, LT/D
Wellman-Lord	Toa Nenryo/Arita, Japan	October 1974	1	2/150
Wellman-Lord	Toa Nenryo/Matsushima, Japan	October 1974	1	1/80
Wellman-Lord	Toa Nenryo Refinery/Kawasaki, Japan	August 1971	1	2/200
Wellman-Lord	Standard Oil of California/El Segundo, California	September 1972	1	3/137
Wellman-Lord	Standard Oil of California/El Segundo, California	January 1975	1	1/290
Wellman-Lord	Standard Oil of California Richmond, California	August 1974	1	2/150
SCOT	Champlin Petroleum Company/Wilmington, California	June 1973	1	1/15
SCOT	Douglas Oil Company/ Paramount, California	June 1973	1	1/9
SCOT	Shell Canada, Waterton Gas Treating Plant/ Alberta, Canada	December 1974	1	1/2100
SCOT	British Petroleum Standard Oil of Ohio/ Marcus Hook, Pennsylvania	October 1974	1	1/160
SCOT	U. S. Steel/Clairton, Pennsylvania	Late 1974	-	--
SCOT	Sun Oil Co./Duncan, Oklahoma	Late 1974	-	--
SCOT	Marathon Oil Co./ Detroit, Michigan			--
SCOT	Murphy Oil Co./ Meraux, Louisiana	Late 1974	-	--
SCOT	Shell Oil/Houston, Texas	Late 1974	-	--

Table 4-1. (Cont.) LISTING OF ANNOUNCED TAIL GAS TREATING UNITS FOR CLAUS SULFUR PLANTS AS OF 3/1/74

Type Unit	Company/Location	Onstream Date	No. of Units	Number/Capacity Claus Plant, LT/
IFP	Nippon Petroleum Refining Company (Caltex)/Negishi, Japan	1971	1	1/300
IFP	Idemitsu Oil/Himeji, Japan	1972	1	1/250
IFP	Showa Oil (Shell)/Kawasaki, Japan	1972	1	1/80
IFP	Kyokuto Petroleum Industries (Mobil)/Chiba, Japan	1972	1	1/200
IFP	Chevron Standard Ltd. (Chevron Research)/Nevis, Alta., Canada	1972	1	1/260
IFP	Mitsubishi Oil Company (Getty)/ Mizushima, Japan	1972	1	1/180
IFP	Mitsubishi Oil Company (Getty)/ Mizushima, Japan	1972	1	1/350
IFP	Phillips Petroleum/ Borger Texas	1973	1	1/45
IFP	Ministry of Gas/Orembourg I, U.S.S.R.	1974	1	1/800
IFP	Ministry of Gas/Orembourg II, U.S.S.R.	1974	1	1/800
IFP	Ministry of Gas/Orembourg III, U.S.S.R.	1974	1	1/800
IFP	Stauffer Chemical Company/ Delaware City, Del., U.S.A.	1973	Confidential	Confidential
IFP	Commonwealth Oil Refining/ Ponce, Puerto Rico, U.S.A.	1973	1	1/60
IFP	Koa Oil No. 1/Marifu, Japan	1973	-	--
IFP	Phillips/Sweeny, Texas	1973	1	1/45
IFP	Koa Oil No. 2/Marifu, Japan	1974	-	--
IFP	Unannounced/	1975	-	1/400

4.3 PERFORMANCE OF EMISSION CONTROL SYSTEMS

The Wellman-Lord, IFP-2, Beavon, SCOT and Cleanair processes all guarantee sulfur emissions less than 200-300 ppmv, for an overall sulfur recovery including the Claus sulfur plant of better than 99.9 percent. The Sulfreen and IFP-1 are capable of reducing sulfur emissions to 1500-3000 ppm, for an overall 99.0 percent sulfur recovery including the Claus sulfur plant.

Table 4-2 summarizes the expected concentration and mass emissions as discussed above both for emission control systems on a 100-long-ton-per-day Claus sulfur plant. Uncontrolled emissions are also included for comparison.

Emission Source Test Results

Four processes--the IFP-1, Wellman-Lord, SCOT and Beavon--were tested to determine emissions of SO_2, H_2S and reduced sulfur compounds (H_2S, COS and CS_2). The data gathered by these tests are presented in Figures 4-9 through 4-12. The data represented by black circles is data gathered by the Agency, while the data represented by white circles is data gathered by refinery personnel or the LA APCD.

Figure 4-9 summarizes the results obtained from an emission test on the IFP-1 process. This process was not operating on a petroleum refinery sulfur recovery plant, but was operating on a large Claus sulfur plant installed in a carbon disulfide plant. The data, however, is applicable to refinery sulfur plants and the emission levels achieved representative of what would be achieved by the IFP-1 process on a refinery sulfur plant. As shown in Figure 4-9, emissions of SO_2 ranged from 2300 to 2600 ppm.

Table 4-2. CALCULATED EMISSIONS FROM SULFUR RECOVERY PROCESSES IN PETROLEUM REFINERIES
(Basis: 100 long tons/day sulfur plant, 90% H_2S fed)

Process	Overall Sulfur Removal Efficiency	Emissions ppmv, (lb/hr)					
		H_2S	SO_2	S_8 Vapor	COS	CS_2	Total as SO_2
2 or 3 Stage Claus	95	6000 (200)	3000 (150)	500 (120)	500 (30)	400 (30)	14,000 (900)
Claus + Incinerator[a]	95	trace --	8000-10,000 (900)	-- --	trace --	trace --	8000 (900)
Claus + IFP-1[a]	99.0	trace --	2000 (190)	-- --	trace --	trace --	2000 (190)
Claus + Sulfreen[a]	99.0	trace --	2000 (190)	-- --	trace --	trace --	3400 (190)
Claus + SCOT[a]	99.9	trace --	200 (14)	-- --	trace --	trace --	200 (14.0)
Claus + Beavon	99.9+	<10 --	-- --	-- --	75 (3.0)	75 (5.0)	225 (11)
Claus + Cleanair	99.9+	<10 --	-- --	-- --	75 (3.0)	75	225 (11)
Claus + Wellman-Lord	99.9	trace --	250 (20)	-- --	trace --	trace --	250 (20)
Claus + IFP-2	99.9	trace --	250 (20)	-- --	trace --	trace --	250 (20)

Notes

[a] Levels shown after final incineration step.

Figure 4-9. Sulfur Dioxide Emissions
IFP-1 Process[25]

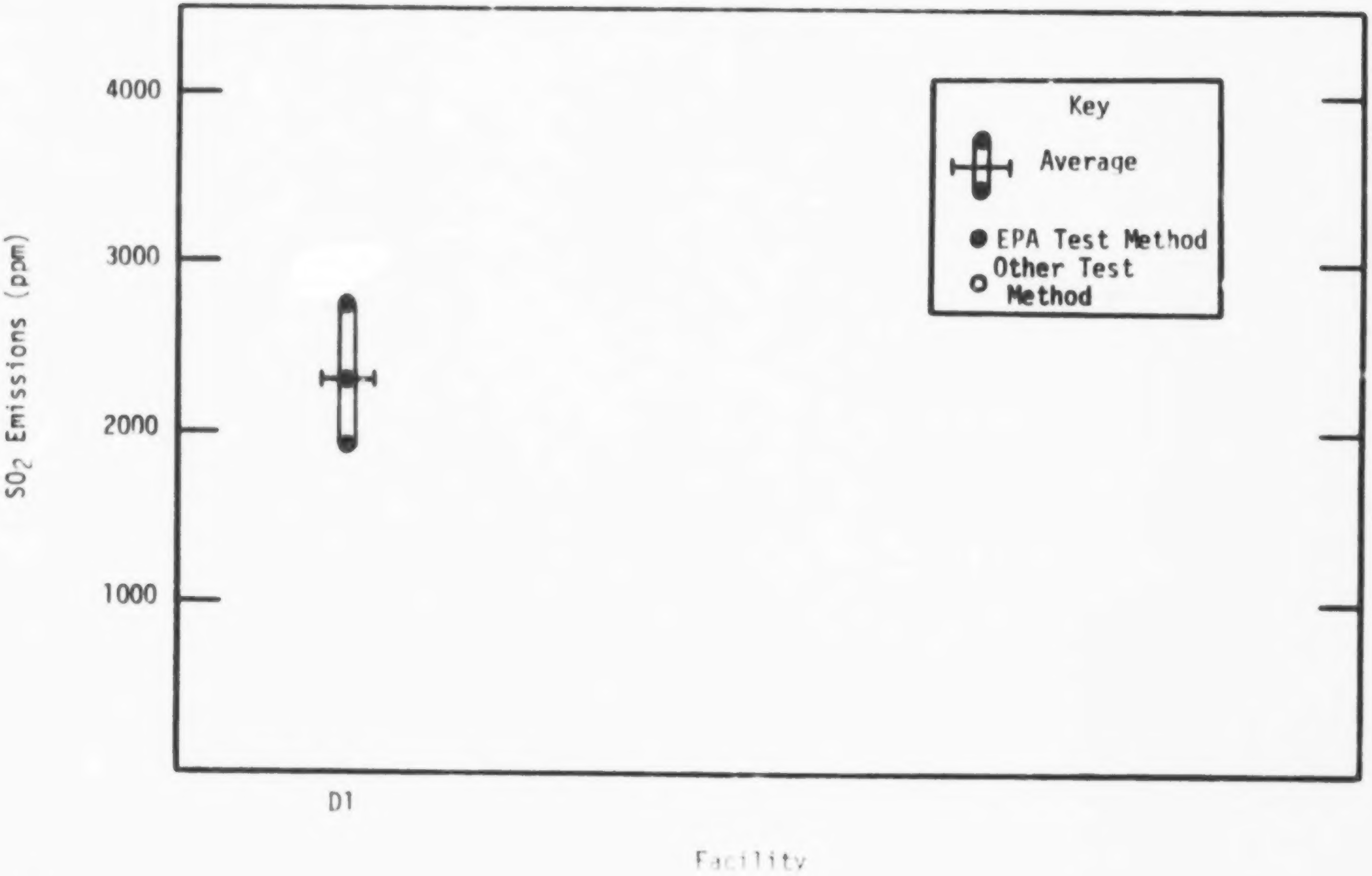


Figure 4-10 summarizes the results obtained from emission tests on a Wellman-Lord process and a SCOT process. Test B1 was conducted by the Agency, test B2 was conducted by refinery personnel and tests B3 and C3 were conducted by the LA APCD. The Wellman-Lord process is an oxidation-scrubbing process, while the SCOT process is a reduction-scrubbing process followed by incineration. Emissions of SO_2 from the Wellman-Lord process ranged from 10 to 50 ppm and emissions from the SCOT process averaged 210 ppm.

Figures 4-11 and 4-12 summarize the results obtained from emission tests on the Beavon process. Test B1 was conducted by the Agency, test B2 was conducted by refinery personnel, and Tests B3, E3 and F3 were conducted by the LA APCD. Emissions of H_2S were undetectable in four of these tests and ranged from 0 to 7 ppm in the fifth. Emissions of reduced sulfur compounds (calculated as SO_2) generally ranged from 10 to 20 ppm in each of these tests.

Vendor Guarantees

Vendors of the higher efficiency tail gas treatment processes normally guarantee emissions of total sulfur, expressed as SO_2 equivalent, not to exceed 200 to 500 ppmv. [SO_2 equivalent is equal to (SO_2 + H_2S + COS + $2CS_2$ + sulfur vapor) expressed in gas concentrations only.] The J.F. Pritchard Company designed the Cleanair tail gas process not to exceed 200 ppmv, 250 ppmv, and 300 ppmv total sulfur emissions for their first three installations.[26,27,28] Union Oil Research designed the initial Beavon units not to exceed

Figure 4-10. Sulfur Dioxide Emissions
Wellman-Lord Process[29,30,31]
SCOT Process[32]

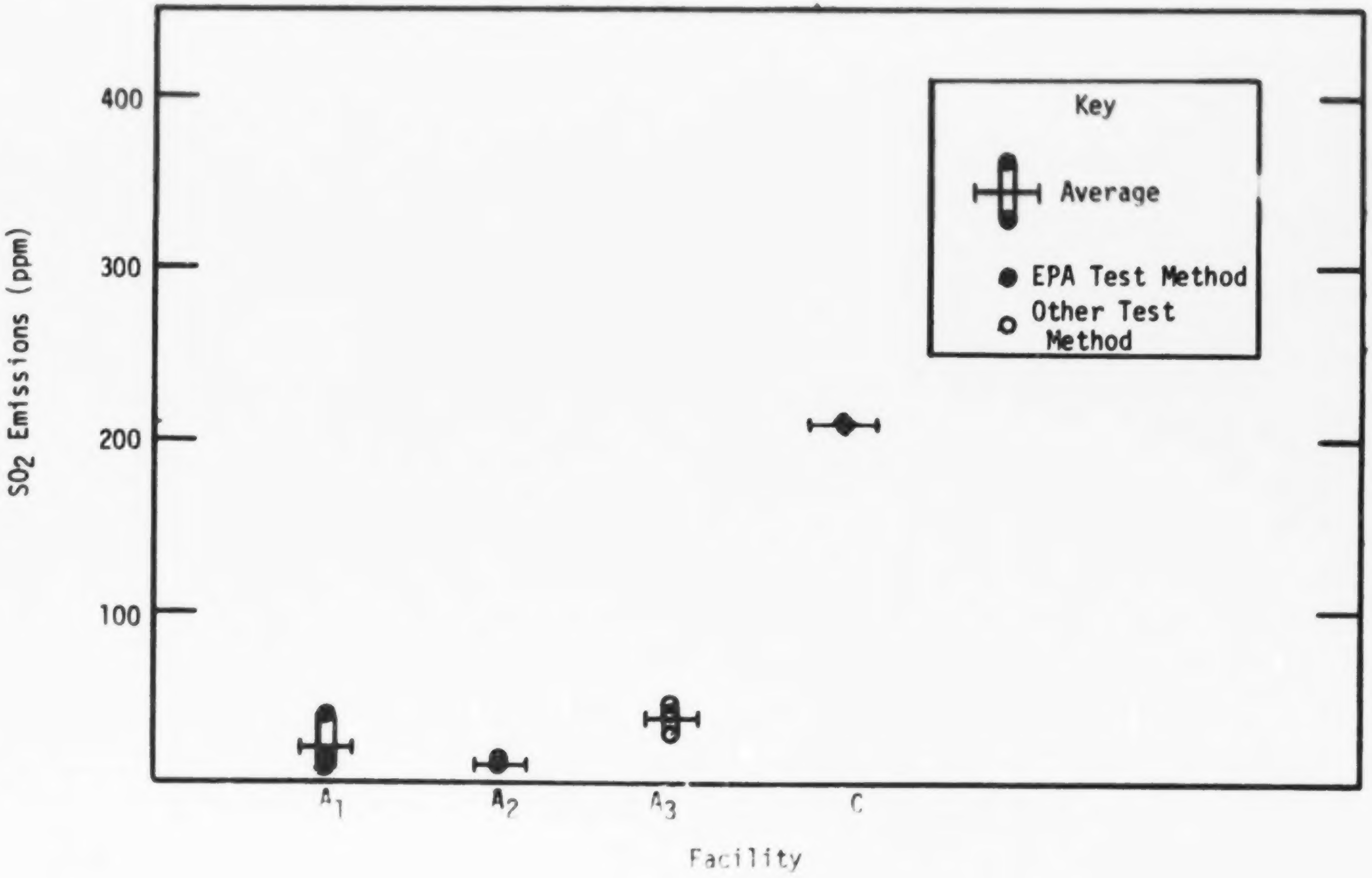


Figure 4-11. Hydrogen Sulfide Emissions[33,34,35]
Reavon Process

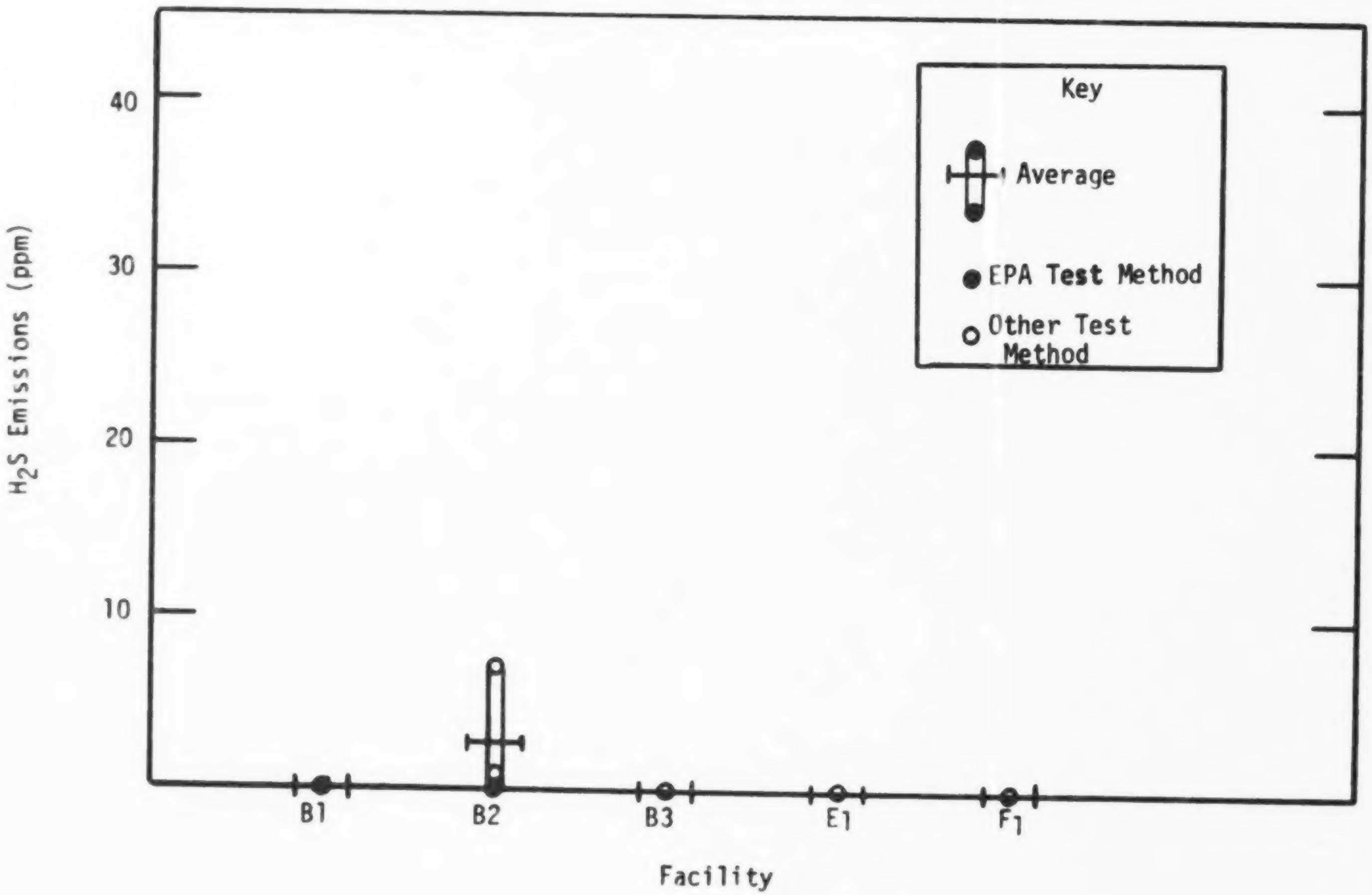
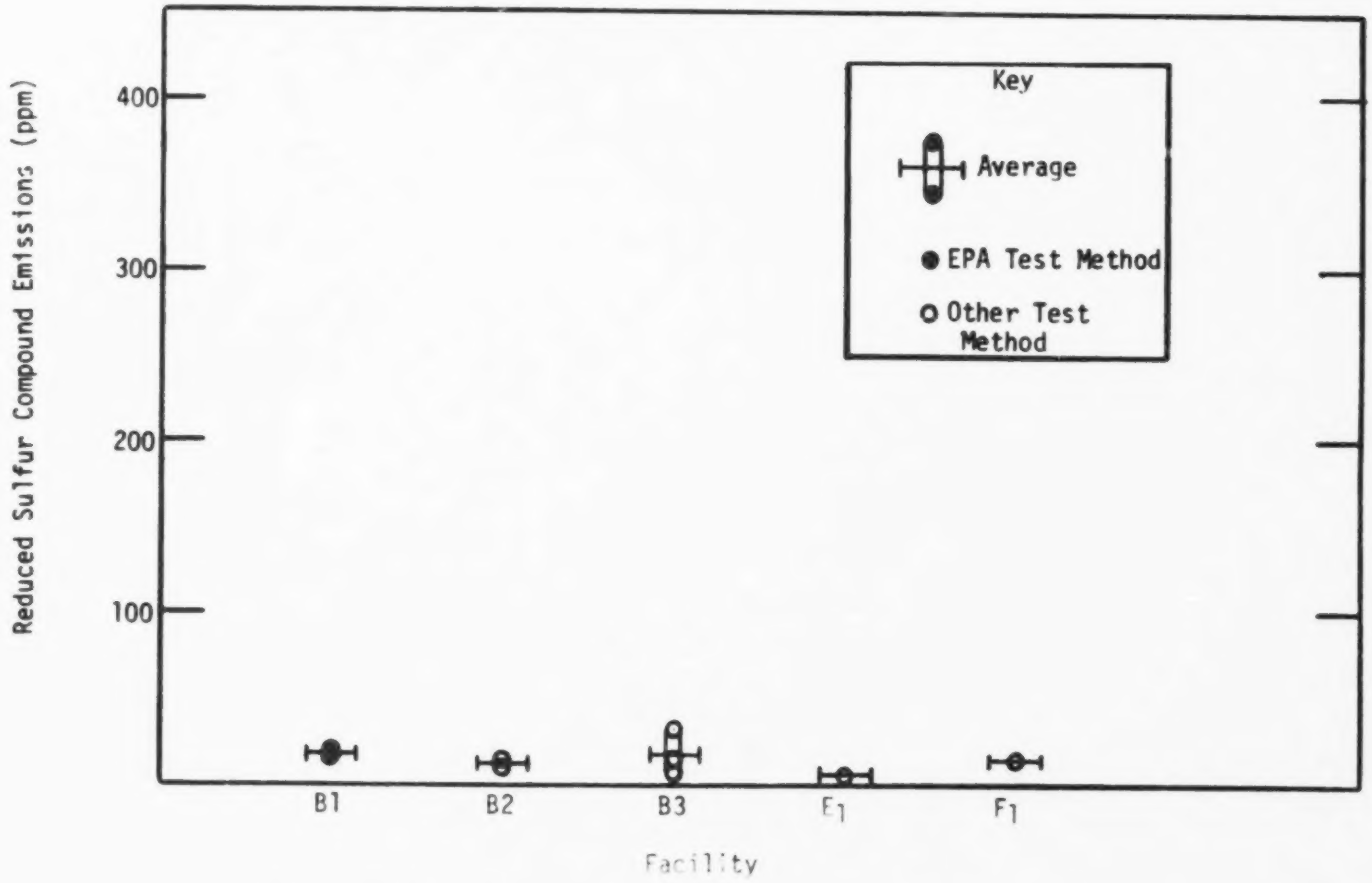


Figure 4-12. Reduced Sulfur Compound Emissions[36,37,38]
Reavon Process



210 ppmv total sulfur emissions.[39] Shell Development gave emission guarantees of 500 and 400 ppmv hydrogen sulfide for their initial installation of the SCOT process, though they have cited guarantees as low as 300 ppmv H_2S (before incineration) in their literature.[40,41,42] Davy Power Gas guaranteed 250 ppmv total sulfur as SO_2 on their first U.S. Claus plant application of the Wellman-Lord system.[43]

Other tail gas processes which do not remove COS or CS_2 usually guarantee efficiencies of H_2S and SO_2 removal. These guarantees cannot be directly correlated to a total sulfur emission guarantee because the concentrations of COS and CS_2 vary according to Claus feedstock composition and operating conditions in the first stage catalytic converter. An example of vendor emission guarantees is the IFP guarantee at one installation of 90 percent removal of $H_2S + SO_2$ in Claus tail gas.[44]

Neither of the vendor guarantees specified whether the concentrations quoted were on a dry or wet basis or whether they were adjusted to zero percent oxygen. Therefore, the final levels of H_2S and SO_2 could differ from the guaranteed levels when these conditions are taken into account.

4.4 REFERENCES

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2. Barthel et. al., "IFP Processes for Recovering H_2S and SO_2 from Claus Unit Tail Gas and for Cleaning SO_2 from Stack Gas," APCA Paper 73-304.

3. Reference 1, pp. 84-90.

4. Krill, H. and Storp, K., "H_2S Adsorbed from Tail Gas," Chemical Engineering 80(17), pp. 84-85, (July 23, 1973).

5. Reference 1, pp. 52-55.

6. Potter, Brian H., and Earl, Christopher B., "The Wellman-Lord SO_2 Recovery Process," presented to the 1973 Gas Conditioning Conference.

7. Reference 1, pp. 68-71.

8. Reference 2.

9. Reference 1, pp. 43-49.

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5. MODIFICATION AND RECONSTRUCTION

Existing sources which are modified may become subject to standards of performance under section 111 of the Clean Air Act. Any physical or operational change to an existing facility which results in an increase in the emission rate of any pollutant to which a standard applies may cause that facility to be considered a modified source, subject to compliance with standards of performance. The full discussion of modification is included under Subpart A - General Provisions of Part 60, 40 CFR.

5.1 MODIFICATION OF REFINERY SULFUR PLANTS

Under the General Provisions of Part 60 40 CFR, physical changes to a facility resulting from routine maintenance, repair or replacement will not be considered modifications. Also, neither an increase in production capacity if this does not require a capital expenditure,as defined by §60.2(bb); nor the use of alternative raw materials, if the facility was originally designed to accommodate materials, will be considered modifications.

The H_2S gases processed in refinery sulfur plants are produced throughout a petroleum refinery in a number of different process units. Consequently, almost any change within a petroleum refinery,such as a change in the type of crude oil processed, construction of new refinery process units, expansion of existing process units, or even a change in the operation of various process units, could potentially lead to a modification of an existing refinery sulfur plant.

Changes such as these could increase the volume of H_2S gases generated within the refinery, leading to a need for increased sulfur recovery capacity. Most refinery sulfur plants, however, are overdesigned to some extent in anticipation of fluctuations in the volume of H_2S gases generated within the refinery due to seasonal changes in refinery operation (i.e., maximum fuel oil production in the winter months compared to maximum gasoline production in the summer months), or to changes in the types of crude oil processed. As a result, most refinery sulfur plants have excess sulfur recovery capacity and can readily accommodate changes within the refinery which require only moderate increases in sulfur recovery capacity.

Where the increased volume of H_2S gases is more than that which can be readily accommodated by existing sulfur plants, additional plants have usually been constructed rather than expanding existing plants. While some expansion of existing sulfur recovery plants would be possible through operation at higher pressure, this would also probably require addition of another Claus catalyst stage to compensate for the unfavorable shift in the equilibrium of the Claus reaction which would accompany an increase in pressure. In addition, alterations to the existing furnace and sulfur condensers would probably also be necessary to provide increased combustion capacity and increased sulfur condensation capacity. As a result, the expense and problems associated with expansion of existing sulfur recovery plants, plus the desire on the part of many petroleum refineries to have excess sulfur recovery capacity and more than one sulfur plant to compensate to some extent for the shut-down of a sulfur recovery plant due to a malfunction, has led refineries to construct additional sulfur recovery plants rather than expand existing ones.

Although as discussed in Chapter 3 the efficiency of sulfur recovery in Claus plants and hence emissions from sulfur plants are dependent on the composition of the H_2S gases processed (lower concentrations decrease efficiency), changes within petroleum refinereies such as those mentioned earlier do not lead to significant changes in the composition of the H_2S gases processed by refinery sulfur plants. The amine treating units which remove H_2S from the gases generated by various refinery process units essentially recover a gas stream containing 80-90 percent H_2S regardless of the H_2S content of the original process gas.

Occasionally, however, in response to local or state air pollution control regulations, petroleum refineries have been required to control sour water stripper gases in refinery sulfur plants. These gases usually contain only 30-40 percent H_2S and similar concentrations of ammonia. In some refineries the total volume of these gases can be about the same as the total volume of H_2S gases produced by the amine treating units. If any of these gases are mixed with those from the amine treating units, the concentration of H_2S in the gases processed by the sulfur plant is lowered. In addition, since the ammonia present in the sour water stripper gases results in the formation of ammonia sulfates in a Claus plant which can lead to fouling of the Claus catalyst, the ammonia has to be removed by incineration of the sour water stripper gases. This contributes to even greater dilution of the gases processed by the sulfur plant because of the fuel and air required for incineration.

Consequently, if sour water stripper gases are mixed with the H_2S gases produced by the amine treating units in a refinery to any appreciable extent and fed to an existing sulfur recovery plant, emissions from the sulfur plant would increase as a result of both the higher sulfur throughput and the resulting decrease in sulfur recovery efficiency. Whether or not this would be termed a modification would depend on the circumstances involved. If prior to introduction of the sour water stripper gases into the sulfur plant they were incinerated and vented to the atmosphere, SO_2 emissions from the refinery as a whole would decrease. Under the general provisions of 40 CFR Part 60, in this situation the sulfur plant would not be considered as a modified source even though its emissions would have increased.

If, however, these sour water stripper gases had not been incinerated and vented to the atmosphere prior to their introduction into the sulfur recovery plant, this might be considered a modification. If the sulfur recovery plant required alterations to accommodate these gases, such as changes to the Claus furnace which required a capital expenditure to carry out, then this would be considered a modification and the sulfur recovery plant would be subject to compliance with standards of performance. If, on the other hand, the sulfur recovery plant required no alteration to accommodate these gases, the decision as to whether this was a modification would hinge on the question..."Is this a change in the method of operation?" (i.e., was the sulfur plant originally designed to process these gases?). If this was concluded to be a change in the method of operation, the sulfur recovery plant would be considered a modified source subject to compliance with standards of performance.

The emission control techniques discussed in Chapter 4 are as applicable to modified refinery sulfur plants as they are to new refinery sulfur plants, since these control techniques are essentially "add-on" control techniques which operate independently of the refinery sulfur plant. In addition, the potential modifications of refinery sulfur plants discussed above would not significantly change the characteristics of the tail gas from the sulfur plant and thus would not prevent the use of any of the control techniques discussed in Chapter 4. While the Cleanair process might require a catalyst change in the first stage catalyst reactor of a modified refinery sulfur plant to reduce formation of COS and CS_2, and the IFP-1 or the Sulfreen process might require the installation of additional instrumentation and process controls to ensure maintenance of the proper H_2S/SO_2 ratio in the tail gas from the sulfur plant, these requirements are minor and could be readily accommodated in a modified refinery sulfur plant. The Wellman-Lord, Beavon or SCOT processes, however, could be installed as readily on a modified refinery sulfur plant as on a new sulfur plant. Each of these emission control techniques, therefore, can be expected to function as well on modified existing refinery sulfur plants as on new refinery sulfur plants and emissions could be reduced to the same levels in both situations.

5.2 RECONSTRUCTION OF REFINERY SULFUR PLANTS

Under the General Provisions of Part 60 40 CFR, existing sources which are reconstructed may be considered as new sources subject to compliance with standards of performance, regardless of whether emissions increase or not. An existing source will be considered reconstructed, however, only if most of the separate components of the source are replaced.

An incremental expansion of a refinery sulfur plant, therefore, is more likely to be considered a potential modification than a reconstruction. In those cases where the desired increase in sulfur plant capacity would be sufficient to necessitate replacement of most of the separate components of an existing sulfur plant, it would probably be more economical to maintain the capacity of the existing plant and construct a new plant to provide the additional capacity as discussed above.

Construction of an additional catalyst/sulfur condenser stage to an existing refinery sulfur plant to increase efficiency would not be considered reconstruction. If sulfur capacity were increased at the same time with a resulting increase in emissions, however, this would probably be considered a modification.

As with modified refinery sulfur plants, each of the emission control techniques discussed in Chapter 4 are as applicable to reconstructed sulfur plants as to new sulfur plants. Consequently, emissions could be reduced to the same levels through the use of these control techniques whether the refinery sulfur plants were new or reconstructed.

6. EMISSION CONTROL SYSTEMS

Based on the discussion presented in the preceding chapters, two alternative emission control systems emerge as possible candidates to serve as the basis for standards of performance (i.e., the best system of emission reduction). These systems are the low temperature Claus reactor system and the tail gas scrubbing system.

6.1 LOW TEMPERATURE CLAUS REACTOR SYSTEM

As indicated previously, most sulfur recovery plants are two- or three-stage Claus units which generally achieve a sulfur recovery efficiency of about 95%. A low temperature Claus reactor system may be added to achieve an improvement in overall sulfur recovery. The low temperature Claus catalyst reaction system is much more complex than a conventional Claus reaction stage and it increases overall sulfur recovery efficiency to about 99%. Emissions are reduced by about 80 to 85% over those from conventional Claus plants. Like the conventional Claus, the emissions from the low-temperature system consist essentially of SO_2. Incineration of the tail gases prior to release to the atmosphere effectively converts any H_2S remaining, and any COS and CS_2 formed in the Claus reactors, to SO_2.

As with the conventional two- or three-stage Claus unit, the low-temperature Claus reactor system depends on maintenance of the proper H_2S/SO_2 ratio in the gases in the sulfur plant. Consequently, minor fluctuations in the gases processed by a Claus sulfur plant that would not lead to a significant increase in emissions from a conventional two- or three-stage unit are likely to result in an appreciable increase in emissions from a low-temperature Claus reactor system. The problem of maintaining a 99% overall sulfur removal efficiency, therefore, is more difficult than maintaining a 95% overall sulfur removal efficiency. Hence, emissions from a low-temperature Claus reactor system are likely to exhibit considerably more fluctuation than those from a two- or three-stage conventional Claus unit, although the absolute magnitude of emissions would be much lower.

6.2 TAIL GAS SCRUBBING SYSTEM

As discussed in Chapter 4, two different types of tail gas scrubbing systems may be used to reduce emissions from Claus sulfur plants--reduction/scrubbing systems or oxidation/scrubbing systems. Either type of system increases overall sulfur recovery to about 99.9 percent, thereby reducing emissions from a conventional two- or three-stage Claus sulfur plant by about 98-99 percent.

The Beavon, Cleanair and SCOT processes discussed in Chapter 4 are representative of the reduction/scrubbing systems. In these systems the tail gases from the final sulfur condenser of a conventional Claus sulfur plant are reduced through the use of a reduction catalyst. Essentially all the SO_2 and about 80-85 percent of the COS and CS_2 is converted to H_2S. In the Beavon and Cleanair processes the H_2S is then absorbed in a scrubbing solution and converted directly to sulfur via the Stretford process (see Chapters 3 and 4).

In the SCOT process the H_2S is absorbed in a scrubbing solution, then desorbed and recycled back to the Claus sulfur plant.

The Wellman-Lord and IFP-2 processes are representative of the oxidation/scrubbing systems. In these systems the tail gases from an incinerator following the final sulfur condenser of a conventional Claus sulfur plant are absorbed in an SO_2 scrubbing system. The SO_2 is then regenerated and in the Wellman-Lord process recycled to the Claus sulfur plant. In the IFP-2 process the SO_2 is mixed with a small bypass gas stream from the H_2S gases processed by the sulfur plant and then sent to a low temperature Claus catalyst reactor. The off-gases from the low temperature Claus reactor are then recycled to the Claus plant incinerator.

Emissions from the oxidation/scrubbing systems are essentially SO_2. Incineration of the tail gases from the Claus sulfur plant prior to entering the SO_2 scrubbing system effectively converts any H_2S, COS and CS_2 to SO_2. Emissions from the reduction/scrubbing systems, however, can be either SO_2 or a mixture or H_2S, COS and CS_2, depending on whether the tail gases from the scrubbing system are incinerated before discharge to the atmosphere. Reduction of the tail gases from the final sulfur condenser of a Claus sulfur plant effectively converts all the SO_2 to H_2S, but only about 80-85 percent of the COS and CS_2 present is converted to H_2S. The COS and CS_2 remaining is not absorbed in the H_2S scrubbing system and is, therefore, released to the atmosphere in the tail gases as COS and CS_2 along with some H_2S, unless these gases are first incinerated.

Incineration effectively converts the COS, CS_2 and H_2S present to SO_2. Incineration of the tail gases before discharge to the atmosphere is the final step of the SCOT process, but it is not part of the Beavon or Cleanair processes.

Maintaining the overall sulfur recovery efficiency of 99.9 percent provided by tail gas scrubbing systems installed on Claus sulfur plants is actually less of a problem than maintaining the lower efficiency provided by the low-temperature Claus reactor system. As discussed above, this system depends on maintenance of the H_2S/SO_2 ratio in the Claus catalyst reactors at 2/1 to achieve the level of overall sulfur recovery efficiency of which it is capable. Consequently, emissions from this system are sensitive to fluctuations that tend to upset this ratio.

The tail gas scrubbing systems, however, do not depend on maintaining this ratio of H_2S/SO_2. Regardless of what the ratio of H_2S/SO_2 may be in the tail gases from the sulfur plant, all the H_2S is converted to SO_2 and absorbed in an SO_2 scrubbing system, or all the SO_2 is converted to H_2S and absorbed in an H_2S scrubbing system. Neither type of tail gas scrubbing system, therefore, is sensitive to fluctuations in the gases processed by the sulfur plant and in operation, these systems serve to dampen out fluctuations. Consequently, fluctuations in emissions from these tail gas scrubbing systems are minimal and an overall sulfur recovery of about 99.9 percent is achieved under essentially all normal operating conditions.

7. ENVIRONMENTAL IMPACT

Refinery sulfur plants are major point sources of sulfur dioxide emissions within petroleum refineries. As discussed in Chapter 3, these emissions result from treatment of the gases produced by various sulfur removal processes within the refinery. A typical uncontrolled sulfur plant (two- or three-stage Claus plant) recovers about 95% of the sulfur in the incoming gas stream. Thus, emissions of sulfur dioxide are usually in the range of 8,000 to 10,000 ppm. The objective of new source performance standards is to limit these emissions. As discussed in Chapter 6, two alternative emission control systems have been identified as candidates for the best system of emission reduction: various low temperature extended Claus reaction systems and a number of tail-gas scrubbing systems. The extended Claus reaction systems result in residual emissions of SO_2. The tail-gas scrubbing systems employ oxidation or reduction processes and result in residual emissions of SO_2 (oxidation) or H_2S, COS, and CS_2 (reduction). The reduction system generally, however, leads to the overall lowest level of emissions.

In assessing the environmental impact associated with standards of performance for refinery sulfur plants, the degree of emission control achieved by each alternative emission control system which could serve as the basis for standards needs to be compared not only against emissions from uncontrolled plants, but against emissions from plants controlled to meet State Implementation Plan (SIP) regulations. Other facets of environmental impact, such as potential water pollution, solid waste generation and energy consumption also need to be assessed in the same manner.

As discussed in Chapter 3, most SIP's require new refinery sulfur plants to achieve an overall sulfur recovery of 99 percent. This requires a level of emission control equivalent to emission control alternative I. A few SIP's, however, require an overall sulfur recovery of only 96 percent. This level of sulfur recovery can be achieved by conventional three-stage Claus plants which, from the point of view of this document, are considered to represent uncontrolled plants. Similarly, a few local air pollution control agencies require an overall sulfur recovery of 99.9 percent. This is equivalent to emission control alternative II. Finally, a number of states which contain no refineries or oil and gas production facilities located within their borders have no air pollution regulations limiting emissions from refinery sulfur plants.

7.1 Ambient Air Quality Impact

The health and welfare effects of SO_2 have been well documented.[1] The health and welfare effects of H_2S, COS and CS_2, however, are not as well documented as those of SO_2. Table 7.1 summarizes the major health and welfare effects known to result from exposure to various levels of these pollutants. Of the three (H_2S, COS, and CS_2), H_2S appears to be the most harmful. It can lead to death at concentrations exceeding 1,500,000 $\mu g/m^3$ while continuous exposure to concentrations as low as 15,000 $\mu g/m^3$ leads to

Table 7.1

Health and Welfare Effects of Exposure to H_2S, CS_2 and COS

Pollutant Concentration ($\mu g/m^3$)	Hydrogen Sulfide (H_2S)[a]		Carbon Disulfide (CS_2)[a]		Carbonyl Sulfide (COS)[a]	
	Human Health	Animals, Materials, Plants	Human Health	Animals, Materials, Plants	Human Health	Animals, Materials, Plants
4	No reported effect	Tarnishing of silver and copper after 40 hrs.				
45	Odor threshold			(Unknown)	(Unknown)	(Unknown)
75		Discoloration of metallic paints after 2 hrs.				
500	Definite perception of smell					
3,500		Injury to certain crops such as alfalfa, barley and cotton	Odor threshold	(Unknown)	(Unknown)	(Unknown)
14,000			Disruption of reproductive processes in women			
15,000	Eye irritation					
30,000	Max. allowable occupational exposure (ACGIH)		Max. allowable 8 hr occupational exposure (ACGIH)			
75,000				(Unknown)	(Unknown)	(Unknown)
150,000	Olfactory fatigue in 2-5 min. Death in 8-48 hrs.					
400,000	Dangerous after 30 min.	Injury to most plants				
800,000	Death after 30 min.		Slight narcotic effect on nervous system after a few hours	(Unknown)	(Unknown)	(Unknown)
1,500,000	Immediate loss of consciousness followed by rapid death	50% injury to tobacco plants after 100 min., tomatoes after 30 min.				
2,400,000						No effect noted on laboratory rabbits
3,200,000			Serious narcotic effect on nervous system after 30 min.	(Unknown)	(Unknown)	Death of laboratory rabbits after 35 min.
10,000,000			Dangerous after 30 min.			
15,000,000			Death after 30 min.			

Notes:

[a] Reference 2.

symptoms such as conjunctivitis, sleeplessness, and pain in the eyes. For occupational exposure the American Conference of Governmental Industrial Hygienists (ACGIH) has set a 4-hour-per-week exposure limit of 15,000 $\mu g/m^3$. The effects of H_2S on domestic animals parallel those on humans, while appreciable damage to plants may occur at lower concentrations. H_2S will also cause significant damage to materials, especially metallic and painted surfaces. Metals, such as silver or copper, will be tarnished when exposed to levels as low as 4 $\mu g/m^3$.[2]

Experience with the use of CS_2 in the textile and rubber manufacturing industries, and to a lesser degree from toxicological studies, has shown it to be highly toxic at concentrations approaching 1,000,000 $\mu g/m^3$. Workers exposed to lesser concentrations over a number of years have experienced a variety of symptoms, including mental illness, coronary heart disease, high blood pressure, and changes in normal reproductive processes in women (i.e. disruption of the menstrual cycle and pathological changes in the cellular composition of vaginal smears). Some of these effects have been observed with industrial exposures as low as 14,000 $\mu g/m^3$. The ACGIH limit for occupational exposure to CS_2, however, has been established at 67,857 $\mu g/m^3$. It should be noted that several countries have established lower occupational exposure limits, including the USSR where it is set at 4553 $\mu g/m^3$.[3,4]

Comparatively little information is available relative to the effects of COS. It appears, however, that this compound is less toxic than H_2S or CS_2. One study using laboratory rabbits indicates the lethal dosage is about twice that of CS_2.[4]

To assess the environmental impact associated with standards of performance for refinery sulfur plants, the maximum impact on ambient air quality of emissions from sulfur recovery plants was analyzed. The dispersion model used for estimating maximum ambient air concentrations for averaging times ranging from one hour to one year was the Single Source (CRSTER) Model developed by EPA's Meteorology and Assessment Division. Concentration estimates were extrapolated from the Single Source Model estimates for averaging times less than one hour.

The meteorological input to the Single Source Model consists of one year of hourly stability-wind-temperature data from Houston and Chicago, two major petroleum refining cities. The emission source model is a 100 LT/D Claus plant with a stack height of 50 meters, which would likely accompany a refinery capacity of about 100,000 BBL/day.

In addition to assuming that emissions are from a single stack, it was also assumed that fugitive emissions do not exist, and adverse downwash phenomena (which sometimes occur in the lee of stacks or nearby structures) do not occur. If fugitive emissions or downwash problems existed, a special dispersion analysis would be required to estimate the resultant air quality impact. It should be noted in passing that such problems can result in ambient concentrations several times greater than those predicted in this analysis.

Maximum ambient air concentrations (see Table 7.2) were estimated to occur from about 0.6 to 1.6 kilometers from the sulfur recovery plant. The 24-hour and 8-hour maxima will most likely occur on days when there are several hours during which the wind is from a single direction at about 3-7 meters per second and during which a neutral or near-neutral atmospheric stability condition exists. The one-hour

Table 7.2

Estimated Maximum Ambient Air Pollutant Concentrations

Pollutant	Stack Concentration (ppm)	Ambient Air Concentration ($\mu g/m^3$)							
		2-10 sec.	5 min.	15 min.	30 min.	1 hr.	8 hr.	24 hr.	1 yr.
Base Case[1]									
SO_2	9250	-	-	-	-	860	345	175	15
Alternative I									
SO_2	2000	-	-	-	-	180	80	25	5
Alternative II									
Oxidation									
SO_2	300	-	-	-	-	25	11	4	<1
Reduction									
H_2S	10	25	2	1	1	1	-	-	-
COS	100	380	30	15	7	7	-	-	-
CS_2	95	540	35	15	10	10	-	-	-

Note:

1. 100 LT/day refinery sulfur plant. Overall sulfur recovery of 95 percent.

maxima will occur during unstable or slightly unstable atmospheric conditions, accompanied by light wind speeds on the order of 1 to 2 meters per second. The downwind distance to the one-hour maxima will range from about 0.4 to 1.6 kilometers.

For averaging times less than one hour, the peak concentrations will most likely occur under light winds and unstable atmospheric conditions. The peak concentrations listed in Table 7.2 for averaging times of less than one hour will occur approximately 0.5 kilometers from the source.

The predicted maximum ground-level 24-hour and 1-year ambient air concentrations of SO_2 from a typical uncontrolled 100 LT/day sulfur plant are 175 $\mu g/m^3$ and 15 $\mu g/m^3$, respectively. These levels are well below the corresponding national ambient air quality standards (NAAQS) for SO_2 of 365 $\mu g/m^3$ and 80 $\mu g/m^3$, respectively. Based on this analysis, it appears that emissions from uncontrolled refinery sulfur plants will not by themselves, lead to adverse health or welfare effects. It should be kept in mind, however, that emissions from sulfur recovery plants are not the only source of sulfur dioxide emissions from petroleum refineries, and that petroleum refineries themselves are usually located in major industrial areas which normally contain other major sources of sulfur dioxide emissions. Considered from this perspective, it is apparent that uncontrolled refinery sulfur plants are major contributors to high ambient air concentrations of SO_2, accounting for about 50 percent of the 24-hour and about 20 percent of the one-year NAAQS for SO_2 in this analysis.

It appears from Table 7.2 that emission control alternative I (low temperature extended Claus reaction) reduces the maximum 24-hour ambient air SO_2 concentration by a factor of 7 and the maximum one-year ambient air SO_2 concentration by a factor of 3. Alternative II (tail gas scrubbing), on the other hand, reduces these maximum ambient air concentrations to essentially zero for all practical purposes, assuming an oxidation tail gas scrubbing system is employed. If a reduction tail gas scrubbing system is employed, emissions of SO_2 are eliminated. Use of a reduction system, however, leads to emissions of H_2S, COS and CS_2 which results in low ambient air concentrations of these pollutants.

Specifically, alternative I reduces the maximum 24-hour ambient air SO_2 concentration to 25 $\mu g/m^3$ and the maximum one-year ambient air SO_2 concentration to 5 $\mu g/m^3$. If an oxidation system is employed, alternative II reduces the maximum 24-hour and one-year ambient air SO_2 concentrations to 4 $\mu g/m^3$ and <1 $\mu g/m^3$, respectively.

If a reduction system is employed, alternative II leads to maximum 2-10 second ambient air concentrations of H_2S, COS and CS_2 of 25, 380 and 540 $\mu g/m^3$ and maximum one-hour ambient air concentrations of 1, 7 and 10 $\mu g/m^3$, respectively. Although the maximum 2-10 second ambient air concentrations of H_2S, COS and CS_2 could lead to odor problems or material corrosion problems if they persisted for longer periods (one to two hours), the ambient air quality modeling indicates these concentrations are only of short duration. As shown in Table 7.2, beyond 2-10 seconds the maximum ambient air concentrations of H_2S, COS and CS_2 decrease rapidly and fall well below the threshold limits for odor or material corrosion problems.

Under normal operation, emissions from the reduction emission control systems are no higher than 10 ppm H_2S and 95-100 ppm for both COS and CS_2 and, as discussed above, the resulting ambient air concentrations of these pollutants will be low enough to ensure that no adverse health or welfare effects arise. Emissions of COS and CS_2, however, may increase considerably, approaching levels as high as 1000 ppm, if the catalysts used in the reduction systems are permitted to deteriorate.[3] However, even at this level these emissions are not likely to result in ambient air concentrations sufficiently high to pose adverse health or welfare effects, based on our present knowledge.

As noted earlier, most SIP's require an overall sulfur recovery equivalent to emission control alternative I. Consequently, standards based on alternative I would have little or no impact on ambient air quality. Only if standards are based on emission control alternative II will there be a beneficial impact on ambient air quality. Based on the growth projections presented in Chapter 8, by 1980 some 8100 LT/day of refinery sulfur plant capacity will be subject to NSPS. Nationwide, therefore, the beneficial impact on ambient air quality of standards in 1980, based on emission control alternative II, would be to reduce emissions by some 55,000 tons per year of SO_2.

7.2 Water Pollution Impact

Petroleum refineries normally discharge large volumes of waste water and can be major point sources of water pollution. The amount of waste water discharged varies greatly from refinery to refinery, however, and depends on both the types of process units within the refinery and the degree of water reuse. The potential water pollution impact of a typical 100,000 bbl/day refinery is summarized in Table 7.3. As this table shows, even with the use of best practical control technology to limit water pollutant discharges, this impact can be significant.

Petroleum refinery Claus sulfur plants by comparison generate an extremely small waste water stream. This stream results from condensation of water vapor contained in the H_2S gases as they flow from the amine scrubbing units to the Claus sulfur plant. Although this sour water condensate normally contains 1500-2000 ppm H_2S and up to 1000 ppm ammonia, the volume of water involved is usually less than 0.25 liter per minute, and this is easily handled in the refinery's waste water treatment facilities. In terms of the example presented above, this is about 0.25 m^3/day, or less than 0.002 percent of the total waste water effluent routinely discharged by a moderate size refinery.

The potential water pollution impact of the two alternative emission control systems outlined in Chapter 6 is negligible. Table 7.4 summarizes the characteristics and flow rates of the various waste water streams discharged by each of these systems. As this table shows, although the volume of waste water discharged by some of these emission control processes is larger than that discharged by the Claus sulfur plant, even in the worst case this is less than 50 liters per minute, which is less than

Table 7.3

Water Pollution Impact of a Typical 100,000 bbl/day Petroleum Refinery[1]

Effluent Flowrate, m^3/day	13,500	
Pollutant Load, kg/day	Raw Water	BPCT[2]
COD	1800	200
BOD_5	4500	1100
TOC	1400	350
TSS	700	150
Oil	700	70
Phenolics	150	1
Ammonia	450	100
Sulfides	20	1

Notes:

1. Development Document for Proposed Effluent Limitations Guidelines and New Source Performance Standards for the Petroleum Refining Point Source Category, Effluent Guidelines Division, Office of Air and Water Programs, Environmental Protection Agency, December 1973, EPA/440/1-73/014.

2. Best practical control technology.

Table 7.4

Potential Water Pollution Impact of
Refinery Sulfur Plant NSPS[1]

	Waste Water Source	Amount Discharged	Waste Water Characteristics
Base Case			
100 LT/D Claus Sulfur	Sour Water Condensate	<0.25 liters/min.	1500-2000 ppm H_2S 1000 ppm NH_3
Emission Control Alternatives			
Alternative I	Catalyst Wash	~28,000 liters/2 years	1% Organic Solvent 25% Alkali Metal Salts 74% Water
Alternative II			
Oxidation/Scrubbing Processes			
Wellman-Lord	Sour Water Condensate	20 liters/min.	pH ~2 25% Sodium Salts 75% Water
	Scrubbing Solution Purge	15 liters/min.	
IFP-2	Sour Water Condensate	20 liters/min.	Same As Above
	Catalyst Wash	~28,000 liters/2 years	Same As Alternative II
Reduction/Scrubbing Process			
Beavon	Sour Water Condensate	45 liters/min.	50 ppm H_2S Trace NH_3
	Scrubbing Solution Purge	5 liters/min.	2% Sodium Salts 98% Water
Cleanair	Sour Water Condensate	45 liters/min.	Same As Above
	Scrubbing Solution Purge	5 liters/min.	Same As Above
SCOT	Sour Water Condensate	45 liters/min.	Same As Above

Note:
1. Reference 1.

0.5 percent of the total waste water effluent routinely discharged by a typical 100,000 bbl/day refinery.

The potential water pollution impact associated with alternative I emission control systems (low temperature extended Claus reaction) is negligible. Although this alternative does not generate additional waste water streams continuously, intermittent waste water streams are generated. After about two years of operation, washing of the catalyst is required to restore catalyst activity. As shown in Table 7.4, some 28,000 liters of water are required and, when discharged, this water contains about 1 percent by weight of the organic solvent for the Claus catalyst (polyalkyene glycol), and about 20-25 percent by weight of the Claus catalyst itself (alkali metal salts). This waste water stream, however, can be easily treated in the refinery waste water treatment facilities to prevent any adverse water pollution impact from arising.

The potential water pollution impact associated with alternative II emission control systems (tail-gas scrubbing), although slightly greater than that associated with alternative I systems, is also negligible for all practical purposes. Generally, the waste water streams generated by the various tail-gas scrubbing processes consist of a sour water condensate, similar to that generated by the Claus sulfur plant, and a purge stream containing either organic or inorganic salts. The amount and composition of these waste water streams varies depending on the particular tail-gas scrubbing process used. The sour water condensate is produced by cooling of the gases prior to the scrubbing tower, and the purge stream is necessary in most cases to prevent a build-up of impurities in the scrubbing solutions.

As shown in Table 7.4, the amount of sour water condensate generated by these tail gas scrubbing processes is in the range of 20 to 45 liters per minute for a 100 LT/day Claus sulfur plant. This stream is usually acidic in nature with a pH of about 2 if an oxidation/scrubbing emission control system is employed. If a reduction/scrubbing system is used, this stream is usually only slightly acidic, containing about 50 ppm H_2S and a trace of ammonia. These streams, however, can be added to the sour water condensate stream discharged by the Claus sulfur plant for treatment in the refinery's waste water treatment facilities.

For a 100 LT/day Claus sulfur plant, the purge stream from an oxidation/scrubbing emission control system, such as the Wellman-Lord process, is in the range of 15 liters per minute. This stream consists essentially of a solution of sodium salts in water and generally has the following composition:[5]

Na_2SO_4	5 percent by weight
$NaHSO_3$	5 percent by weight
Na_2SO_3	15 percent by weight
H_2O	75 percent by weight

This stream could be treated in the refinery waste water treatment system without difficulty, or it could be treated by the NICE process developed by Nittetu Chemical Engineering Ltd.[6] The NICE process recovers the sodium as sodium carbonate (Na_2CO_3) or soda ash, which can be used to provide the necessary make-up sodium sulfite/sodium bisulfite solution to the Wellman-Lord process. Davy Power Gas, the developer of the Wellman-Lord process, is also developing a treatment process for this purge stream.[7] Consequently, disposal of this waste water stream will not lead to any adverse water pollution impact.

Unlike the Wellman-Lord process, the other oxidation/scrubbing emission control system, the IFP-2 process, has no purge stream. This process is essentially an upgraded alternative I process and consists of a third-stage low temperature Claus reactor followed by an ammonia scrubber. The only waste water streams discharged are the sour water condensate stream which is common to all the tail-gas scrubbing processes, and an intermittent waste water stream resulting from washing of the low temperature Claus catalyst every two years as mentioned earlier. Thus, there is essentially no potential water pollution impact associated with use of the IFP-2 process.

The purge stream from a reduction/scrubbing emission control system, such as the Beavon or Cleanair process, installed on a 100 LT/day Claus sulfur plant is in the range of 5 liters per minute. As with the purge stream from the Wellman-Lord process, this stream consists essentially of a solution of sodium salts in water and generally has the following composition:[8]

Na_2CO_3	0.5 percent by weight
$Na_2S_2O_3$	0.5 percent by weight
NaSCN	0.5 percent by weight
Misc. Sodium Salts	0.5 percent by weight
H_2O	98.0 percent by weight

This stream could also be treated in the refinery waste water treatment system without difficulty, or treated by the NICE process to recover the sodium as sodium carbonate. The sodium carbonate could be used to provide the necessary make-up solution to the Stretford scrubbing unit of the Beavon or Cleanair processes. The potential water pollution impact associated with the use of the Beavon or Cleanair processes, therefore, is negligible.

The SCOT process, which is also a reduction/scrubbing emission control system, does not generate a purge stream. As with the IFP-2 process mentioned above, the only waste water stream generated by this process is the sour water condensate stream, which can be added to the sour water condensate stream generated by the Claus sulfur plant for treatment in the refinery's waste water treatment facilities. Thus, use of the SCOT process would result in essentially no water pollution impact.

In conclusion, all the waste water streams generated by the two alternative emission control systems outlined in Chapter 6 can be treated without difficulty in the refinery's waste water treatment facilities. Considering the small amount of waste water discharged by these emission control systems, the potential water pollution impact of NSPS for refinery sulfur plants will be negligible, whether they are based on alternative I or alternative II emission control systems, because of the magnitude of dilution in the refinery's waste water treatment facilities. Also, since these waste water streams are so small, they will have no impact on the ability of petroleum refineries to meet water quality effluent regulations.

7.3 Solid Waste Impact

There is essentially no potential solid waste impact associated with refinery sulfur plant standards based on either alternative I or alternative II emission control systems.

The Claus process itself requires periodic replacement of the reaction catalysts, the frequency of replacement depending upon the impurities present in the acid gas feed. Usually the catalyst, made of bauxite or alumina, is regenerated annually until a substantial loss of activity occurs, normally in two to five years.[9] For a 100 LT/D Claus plant, replacement of the catalyst would require disposal of approximately 70 tons of spent catalyst, usually in landfills. Alumina (aluminum oxide) and bauxite (a natural mixture of iron, aluminum and manganese oxides/hydroxides) are both non-toxic materials. Neither emission control system alternative will affect the rate or quantity of catalyst replacement in the Claus plant.

As for the emission control systems themselves, neither the alternative I systems (low temperature extended Claus reaction) nor the oxidation tail gas scrubbing systems (alternative II) generate any solid waste. The reduction tail gas scrubbing systems, however, do require periodic replacement of the reduction catalysts about every two years.[10] These catalysts usually have significant salvage value, being composed primarily of colbalt-molybdenum, and consequently, are normally returned to a vendor for reprocessing. Hence, even the reduction tail gas scrubbing systems generate essentially no solid waste.

7.4 Energy Impact

Although not generally recognized, petroleum refineries consume a significant amount of energy in processing crude oil into various petroleum products such as petrochemical feedstocks, gasolines, and fuel oils, etc. The energy requirements of a typical moderate or high conversion refinery, for example, usually represent about 10 percent of the crude oil throughput.[11] Thus, the energy consumption of a nominal 100,000 bbl/day refinery is equivalent to about 10,000 bbl/day of fuel oil, or some 250,000 kw-hr/hr.

The energy requirements of refinery sulfur plants are quite small in comparison. A 100 LT/day Claus sulfur plant, for example, typically consumes less than 1000 kw-hr/hr of energy,[12] or less than 0.5 percent of the energy consumed within the petroleum refinery itself. Consequently, the use of Claus sulfur plants to control emissions of sulfur dioxide or hydrogen sulfide at petroleum refineries does not significantly increase the energy requirements associated with petroleum refining.

The energy impact associated with each of the alternative emission control systems outlined in Chapter 6 is summarized in Table 7.5. As this table shows, the impact is negligible in all cases. Alternative I, for example, has a slight energy benefit (i.e. overall energy consumption is reduced somewhat) due to reduced tail gas incineration requirements. Alternative II, on the other hand, has a slight energy penalty or a moderate energy benefit, depending on whether an oxidation or reduction tail gas scrubbing emission control system is employed and on whether tail gas reheat is required to increase plume bouyancy. A few local air pollution control agencies require that gases discharged into the atmosphere must be above a certain minimum temperature to insure good plume bouyancy and thus good plume dispersion. Under these conditions, Alternative II has a slight energy penalty. Most local air pollution control agencies, however, do not have requirements of this nature and in most cases tail gas reheat is not necessary to obtain good plume dispersion. Under these conditions, Alternative II has either a slight energy penalty or a moderate energy benefit, depending on whether an oxidation system or a reduction system is employed. The moderate energy benefit associated with the reduction tail gas scrubbing system arises because of reduced tail gas incineration requirements.

As mentioned earlier in this chapter, most SIP's require new refinery sulfur plants to achieve an overall sulfur recovery of 99 percent. This requires a level of emission control equivalent to alternative I. Consequently, if alternative I is selected as the basis for refinery sulfur plant NSPS, there will be no energy impact associated with the standards.

If NSPS are based on alternative II, there will be either a slight energy penalty or a moderate energy benefit associated with the standards in all but those few localities which already require this type of emission control system. This impact will vary from refinery to refinery depending on whether an oxidation or a reduction tail gas scrubbing system is employed to comply with the NSPS. As shown in Table 7.5, use of an oxidation tail gas

ENERGY IMPACT OF ALTERNATIVE EMISSION CONTROL SYSTEMS

Energy Consumption (Gains)	Base Case[a,c] 100 LT/D Claus Sulfur Plant	Alternative I[1][b,c] Low Temperature Extended Claus Reaction	Alternative II[1][b,c] Tail Gas Scrubbing			
			Oxidation System		Reduction System	
			w/o Reheat	w/ Reheat	w/o Reheat	w/ Reheat
Fuel,[a] MM Btu/hr						
Process	-	-	8.2	8.2	1.7[7]	1.7[7]
Incineration	8.2	6.3	-	5.7[6]	-	5.7[6]
Electricity kw-hr/hr	140	175	300	300	370	370
Steam,[2] lb/hr						
High Pressure[3]	(18,000)	(18,000)	(18,000)	(18,000)	(18,000)	(18,000)
Low Pressure[4]	(7,800)	(7,800)	(4,950)	(4,950)	(7,500)	(7,500)
Total, kw-hr/hr						
With Steam Credit[5]	(894)	(1,049)	(950)	(380)	(1,300)	(735)
Without Steam Credit	960	805	1,120	1,690	540	1,110

Notes
1. Includes energy consumption of Claus sulfur plant.
2. Does not include steam which could be produced if tail gas incinerators were equipped to recover waste heat.
3. Produced at 550 psig and 750°F.
4. Produced at 50 psig and saturated.
5. Conversions to kw-hr/hr as follows:
   Fuel: 10,000 Btu/hr equivalent to 1 kw-hr/hr
   Steam Credit:
     High Pressure: 1,000 lb/hr equivalent to 90 kw-hr/hr
     Low Pressure: 1,000 lb/hr equivalent to 30 kw-hr/hr
6. Incineration of sulfur plant tail gases.
7. Fuel used to produce reduction gases.

a. Reference 12
b. Reference 5.
c. Reference 13.

scrubbing system without tail gas reheat increases the overall energy consumption of a Claus sulfur plant by about 17 percent. Use of a reduction tail gas scrubbing system without tail gas reheat, however, reduces the overall energy consumption by about 50 percent.

Based on the growth projections presented in chapter 8, by 1980 some 8100 LT/day of refinery sulfur plant capacity will be subject to NSPS. Standards based on alternative I will have essentially no impact on national energy consumption, since most SIP's already require the use of this type of emission control system. Standards based on alternative II, however, will reduce national energy consumption by some 54 million kw-hr/yr, or about 90,000 barrels of fuel oil per year, assuming half of the refinery sulfur plant capacity subject to compliance with NSPS install oxidation tail gas scrubbing systems without tail gas reheat and half install reduction tail gas scrubbing systems without tail gas reheat.

7.5 Other Environmental Impacts

No environmental impacts other than those discussed above are likely to arise from standards of performance for refinery sulfur plants, regardless of which alternative emission control system is selected as the basis for standards. Furthermore, other than those resources initially required to construct either alternative emission control system (most of which could probably be salvaged in one way or another), there do not appear to be any irreversible or irretrievable commitment of resources associated with these standards. As discussed above, there is even no overall increase in the energy requirements associated with refinery sulfur plants, since both

Table 7.6

Environmental Impact of No Standards or Delayed Standards

Year	Sulfur Plant Capacity Affected by Standards[1]	Nationwide SO_2 Emissions (M Tons/Yr)			
		No SIP[2]	SIP[3]	Alternative I[3]	Alternative II[4]
1976	3150	130	25	25	2
1977	1425	60	10	10	1
1978	1815	75	15	15	1
1979	850	35	5	5	0.5
1980	850	35	5	5	0.5
TOTAL	8090	335	60	60	5

Note

1. LT/day.
2. 95% control.
3. 99% control.
4. 99.9% control.

emission control systems result in a net reduction in energy consumption.

Based on the growth projections presented in Chapter 8, the adverse environmental impact of no standards or delayed standards on nationwide SO_2 emissions is summarized in Table 7.6. If alternative I is selected as the basis for standards, there is no adverse impact on air quality since alternative I does not reduce emissions beyond levels currently required by most SIP's. If alternative II is selected as the basis for standards, on the other hand, the adverse environmental impact of delaying standards or not setting standards is an increase in nationwide SO_2 emissions of some 5,000 to 25,000 tons per year, reaching a total of about 55,000 tons per year by 1980.

Since there are essentially no adverse water pollution, solid waste disposal or energy consumption impacts associated with either of the alternative emission control systems which could serve as the basis for standards, there is no "trade-off" of potentially adverse impacts in these areas against the resulting adverse impact on air quality of delaying standards or not setting standards. Furthermore, there does not appear to be any emerging emission control technology on the horizon that could achieve greater emission reductions or result in lower costs than that represented by the emission control alternatives under consideration here. Consequently, delaying standards to allow further technical developments appears to present no "trade-off" of higher SO_2 emissions in the near future against lower SO_2 emissions in the distant future.

References

1. "Air Quality Criteria for Sulfur Oxides," U.S. Dept. of Health, Education and Welfare, Public Health Service, January 1969.

2. "Preliminary Air Pollution Survey of Hydrogen Sulfide," U.S. Dept. of Health, Education and Welfare, Public Health Service, October 1969.

3. Peyton, Thomas O., Steele, Robert V. and Mabey, William R., "Carbon Disulfide, Carbonyl Sulfide, Literature Review and Environmental Assessment," EPA Contract 68-01-2940, Task 23, July 1975.

4. Patty, Frank A., Industrial Hygiene and Toxicology, Vol. 2, 2nd Ed., Interscience, New York, 1963.

5. Genco, J.M., and Tam, S.S., "Characterization of Sulfur Recovery from Refinery Fuel Gas," EPA Contract 68-02-0611, June 1974, p. 54.

6. Reference 5, pp. 35, 37-38.

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8. Reference 5, p. 36.

9. Letter, Cole, D.F., J.F. Pritchard and Co. to W.D. Beers, Process Research, Inc. dated June 5, 1972.

10. Reference 5, pp. 52, 57 and 64.

11. "Impact of Motor Gasoline Lead Additive Regulations on Petroleum Refineries and Energy Resources - 1974-1980 Phase 1," EPA Contract 68-02-1332, Task 4, May 1974, p. V-38.

12. Beers, W.D., "Characterization of Claus Plant Emissions," EPA Contract 68-02-0242, Task 2, April 1973.

13. "Comparative Assessment of Coal Gasification Emission Control Systems," EPA Contract 68-01-2942, Task 007, Booze-Allen Applied Research, October 1975.

8. ECONOMIC IMPACT

8.1 INDUSTRY PROFILE

As of April 1975, there were 259 petroleum refineries in the United States with a total capacity of 14.8 million barrels per calendar day (BCD). These refineries ranged in size from 200 BCD to 445,000 BCD, with an average size of approximately 57,300 BCD.[1] In general, new refineries are expected to be considerably larger than the current industry average. Information is available on 12 refineries that have been projected to be built after January 1, 1975. These refineries vary in size from 5,000 BCD to 200,000 BCD, with an average size of approximately 97,000 BCD.[2]

Not all petroleum refineries currently include sulfur recovery plants. At the 259 domestic refineries referred to above, only 81 included sulfur recovery plants. There are currently 122 sulfur recovery plants within the industry, either currently installed or due to be installed in 1975, ranging in size from 4 long tons of sulfur per day (LTD) to 375 LTD, with an average size of 72 LTD.[1,2,3] Sulfur recovery plants tend to be found in the larger refineries. Table 8-1 illustrates this point. For example, there are 175 refineries with individual capacities less than 50,000 BCD, amounting to 67 percent of the total number of 259 refineries. These refineries, however, account for only 16 percent of the total number of 122 sulfur recovery plants. Stated in another way, the average size of a refinery which includes a sulfur recovery plant is approximately 140,000 BCD. This compares to an average size of approximately 27,000 BCD for those refineries without sulfur recovery plants.

Table 8-1. DISTRIBUTION OF SULFUR RECOVERY PLANTS AT DOMESTIC PETROLEUM REFINERIES[1,2,3]
(April 7, 1975)

Refinery Size Increment (BCD)	Number of Refineries	% of Total Number	Number of Sulfur Recovery Plants	% of Total Number
0-50,000	175	67%	19	16%
50,001-100,000	40	15%	33	27%
100,001-150,000	20	8%	23	19%
150,001-200,000	9	3%	20	16%
200,001-250,000	4	2%	8	7%
250,001-300,000	4	2%	9	7%
300,001-350,000	3	1%	6	5%
350,001-400,000	2	1%	-	-
400,001-450,000	2	1%	4	3%
	259	100%	122	100%

Table 8-2 summarizes the current status of the domestic refining industry with regard to sulfur recovery plants. Table 8-3 provides additional detail with regard to the sulfur recovery plants that are currently installed or due to be installed in 1975.

8.2 COST OF ALTERNATIVE EMISSION CONTROL SYSTEMS

As outlined in Chapter 6, there are two alternative emission control systems that could serve as the basis for refinery sulfur plant NSPS. Alternative I, exemplified by the IFP-1 and the Sulfreen processes, achieves an overall sulfur recovery of 99.0 percent measured against the total sulfur in the Claus plant feed gases. Alternative II, exemplified by the Beavon, SCOT, Wellman-Lord, Cleanair, and IFP-2 processes, achieves an overall sulfur recovery of 99.9 percent.

Since more data was available, both from vendors as well as owners, the IFP-1 and the Wellman-Lord and the Beavon processes were taken as representative of the two alternative emission control systems. Costs would have to be comparable for the other systems or they would not be competitive in the marketplace. Tables 8-4, 8-5, 8-6, and 8-7 present the operating costs for the basic Claus sulfur recovery plant, a Claus plant with an alternative I emission control system (IFP-1), a Claus plant with an oxidation alternative II emission control system (Wellman-Lord), and a Claus plant with a reduction alternative II emission control system (Beavon). The plant with the capacity of 10 long tons of sulfur per day is believed to be representative of a unit required by a typical small refinery. The plant with the 100 long ton per day sulfur capacity is believed to be typical of a unit required by a typical large refinery. A plant with a capacity of 5 long tons of sulfur per day, while believed to be too small to be generally utilized in typical refineries, is also shown for comparison.

Table 8-2. SUMMARY OF CURRENT DOMESTIC PETROLEUM REFINERIES[1,3]
(April 7, 1975)

	Number	% of Total Number	Total Capacity (M BCD)	% of Total Capacity	Average Capacity (M BCD)	Capacity Range (M BCD)
Refineries with Sulfur Recovery						
- 95% Recovery	57	22%	7,211	49%	127	12-445
- 99% Recovery	2	1%	184	1%	92	85-99
- 99.9% Recovery	22	8%	2,634	18%	120	29-294
- Total	81	31%	10,029	68%	124	12-445
Refineries without Sulfur Recovery	178	69%	4,816	32%	27	0.33-406
Total Refineries	259	100%	14,845	100%	57	0.33-445

Table 8-3. SUMMARY OF SULFUR RECOVERY PLANTS AT EXISTING DOMESTIC REFINERIES[2,3]
(April 7, 1975)

	Number of Sulfur Plants	% of Total Sulfur Plants	Total Sulfur Capacity (LTD)	% of Total Sulfur Capacity	Average Capacity (LTD)
Refineries with Sulfur Recovery					
- 95% Recovery	94	77%	4,830	57%	51
- 99% Recovery	2	2%	123	1%	62
- 99.9% Recovery	26	21%	3,591	43%	138
- Total	122	100%	8,544	100%	70

Table 8-4. ANNUAL COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH INCINERATION [4,5,6,7,8,9]

(June 1975)

	Plant Size, LTD		
Component	5	10	100
Manpower per Shift	1/2	1/2	1/2
Direct Labor @ \$6.41/hr.	\$28,100	\$28,100	\$28,100
Supv. & Fringes @ 40% DL	11,200	11,200	11,200
Electric Power @ \$0.030/Kwh[(a)]	1,800	3,500	35,300
Fuel @ \$0.60/MCF	2,100	4,100	41,300
Maintenance @ 3% Inv.	22,700	27,200	83,500
Steam Credit @ \$0.50/MLB	(5,400)	(10,800)	(108,400)
Sulfur Credit @ \$25/LT[(b)]	(41,500)	(83,000)	(830,000)
Net Operating Cost	19,000	(19,700)	(739,000)
Capital Charges @ 17% Inv.[(c)]	128,700	153,300	473,100
Total Annual Cost	\$147,700	\$133,600	\$(265,900)
Investment[(d)]	\$757,000	\$902,000	\$2,783,000

Notes:

(a) 350 Operating days per year.

(b) Assumes 95% recovery.

(c) Capital recovery factor for 15 years at 10% interest plus 4% of investment for property taxes, insurance, and G&A.

(d) 6/75 Chem. Eng. Index

Table 8-5. COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH ALTERNATIVE I EMISSION CONTROL SYSTEM AND INCINERATION [4,6,7,9,10,11,12]

(June 1975)

Component	Claus Plant Size, LTD 5	 10	 100
Manpower per shift	1	1	1
Direct Labor @ $6.41/hr	$56,200	$56,200	$56,200
Supv. & Fringes @ 40% DL	22,500	22,500	22,500
Electric Power @ $0.03/KWH[a]	2,200	4,400	44,100
Fuel @ $0.60 MCF	1,600	3,200	31,800
Maintenance @ 3$ Inv. (Claus)	22,700	27,100	83,500
@ 5% Inv. (IFP-1)	4,500	6,300	52,300
Solvent & Catalyst	900	1,700	17,500
Condensate @ $0.30/MGAL	--	--	200
Steam Credit @ $0.50 Mlbs	(5,400)	(10,800)	(108,400)
Sulfur Credit @ $25/LT[b]	(43,300)	(86,600)	(866,300)
Net Operating Cost	61,900	24,000	(666,600)
Capital Charges @ 17% Inv.[c]	144,000	174,800	650,800
Total Annual Cost	$205,900	$198,800	$(15,800)
Investment (Claus)	757,000	902,000	2,783,000
(IFP-1)	90,000	126,000	1,045,000
Total Investment[d]	$847,000	$1,028,000	$3,828,000

Notes:

(a) 350 Operating days per year.

(b) Assumes 99% recovery.

(c) Capital recovery factor for 15 years at 10% interest plus 4% of investment for property, taxes, insurance, and G&A.

(d) 6/75 Chem. Eng. Index

Table 8-6. COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH ALTERNATIVE II EMISSION CONTROL SYSTEM (OXIDATION) [13,14,15]

(June 1975)

Component	Claus Plant Size, LTD 5	10	100
Manpower per Shift	2	2	2
Direct Labor @ \$6.41/hr	\$112,400	\$112,400	\$112,400
Supv. & Fringes @ 40% DL	45,000	45,000	45,000
Electric Power @ \$0.03/KWH (a)	3,800	7,600	75,600
Fuel @ \$0.60/MCF	2,100	4,100	41,300
Maintenance @ 3% Inv. (Claus)	21,900	26,100	82,000
@ 5% Inv. (Wellman-Lord)	18,300	22,500	89,400
Chemicals @ \$200/ton 50% NaOH	3,500	7,000	70,000
Soft Water @ \$0.30/m Gals.	100	200	1,700
Steam Credit @ \$0.50/MLbs	(4,800)	(9,600)	(96,400)
Sulfur Credit @ \$25/LT (b)	(43,700)	(87,500)	(875,000)
Net Operating Cost	\$158,600	\$127,800	(\$454,000)
Capital Charges @ 17% Inv. (c)	186,200	224,400	768,600
Total Annual Cost	\$344,800	\$352,200	\$314,600
Investment (Claus less Incin. (d)	730,000	871,000	2,733,000
(Wellman-Lord)	365,000	449,000	1,788,000
Total Investment (e)	\$1,095,000	\$1,320,000	\$4,521,000

Notes:

(a) 350 operating days per year

(b) Assumes 100% sulfur recovery with tail gas unit.

(c) Capital recovery factor for 15 years at 10% interest plus 4% of investment for property taxes, insurance and G&A.

(d) Incinerator adjustment from, "Air Pollution Control Technology and Costs in Seven Selected Areas," Report No. EPA-450/3-73-010, page 629.

(e) 6/75 Chem. Eng. Index.

Table 8-7. COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH ALTERNATIVE II EMISSION CONTROL SYSTEM (REDUCTION) [8,17,18,19]

(June 1975)

Component	Claus Plant Size, LTD 5	10	100
Manpower per Shift	2	2	2
Direct Labor @ \$6.41/Hr.	\$112,400	\$112,400	\$112,400
Supv. & Fringes @ 40% DL	45,000	45,000	45,000
Electric Power @ \$0.03/KWH[a]	4,700	9,300	93,200
Fuel @ \$0.60/MCF	400	900	8,600
Maintenance @ 3% Inv. (Claus)	21,900	26,100	82,000
@ 5% Inv. (Beavon)	36,300	44,700	141,400
Catalyst & Chemicals	800	1,600	16,300
Soft Water @ \$0.30/MGAL	--	100	600
Steam Credit @ \$0.50/MLBS.	(5,400)	(10,700)	(107,100)
Sulfur Credit @ \$25/LT[b]	(43,700)	(87,500)	(875,000)
Net Operating Cost	172,400	141,900	(482,600)
Capital Charges @ 17% Inv.[c]	247,500	300,100	945,400
Total Annual Charges	\$419,900	\$442,000	\$462,800
Investment (Claus less Incin)[d]	730,000	871,000	2,733,000
(Beavon)	726,000	894,000	2,828,000
Total Investment[e]	\$1,456,000	\$1,765,000	\$5,561,000

Notes:

[a] 350 operating days per year.

[b] Assumes 100% sulfur recovery

[c] Capital recovery factor for 15 years at 10% interest plus 4% of investment for property taxes, insurance and G&A

[d] Incinerator adjustment from "Air Pollution Control Technology and Costs in Seven Selected Areas", Report No. EPA-450/3-73-010, p. 629.

[e] 6/75 Chem. Eng. Index.

Tables 8-8, 8-9, and 8-10 summarize the economics of installing an alternative I or alternative II emission control system on a Claus sulfur recovery plant. For a 100 LTD plant, use of an alternative I system reduces the annual return from $265,900 to $15,800, a loss of $250,100 per year. Use of an alternative II system increases the annual costs to $314,600-462,800, depending on whether an oxidation or reduction process is employed, or a loss of $580,500-728,700 per year. For a 10 LTD Claus plant, use of an alternative I emission control system increases the annual costs to $198,800, a loss of $65,200 per year. Use of an alternative II system increases the annual costs to $352,200-442,000, or a loss of $218,600-308,400 per year. Finally, for a 5 LTD plant, use of an alternative I system increases the annual costs to $205,900, a loss of $58,200 per year, and use of an alternative II system increases the annual costs to $344,800-419,900, or a loss of $197,100-272,200 per year.

8.3 ECONOMIC IMPACT

Impact by Company Size

Two financial profiles have been developed to evaluate the economic impact of the two alternative emission control systems. The first profile represents a large, integrated oil company and the second represents a small oil company. The profile of the large, integrated company is based upon an analysis of the published financial statements of Exxon Corporation, Mobil Oil Corporation, Shell Oil Company, Phillips Petroleum Company, Cities Service Company, and Ashland Oil, Incorporated. These companies considered together should adequately represent the major integrated refiner sector of the domestic oil industry. The resulting financial profile is presented in Table 8-11.

Table 8-8. COMPARISON OF ALTERNATIVE EMISSION CONTROL SYSTEM COSTS FOR A 100 LTD SULFUR PLANT
(Cost Adjusted to June, 1975)

	Total Costs			Differential Over Preceding Case			
Control System	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (lbs/hr)	Unit Cost ($/ton)
Base Case	$2,783,000	(265,900)(a)	932	-	-	-	(5)
Alternative I	3,828,000(b)	(15,800)(b)	187	1,045,000	250,100	745	80(c)
Alternative II							
Oxidation	4,521,000(b)	314,600(b)	19	693,000	330,400	168	468(c)
Reduction	5,561,000(b)	462,800(b)	19	1,733,000	478,600	168	678(c)

Notes:
(a) Denotes gain.
(b) Includes costs of base case Claus sulfur recovery plant.
(c) Incremental costs per incremental ton of SO_2 recovered.

Table 8-9. COMPARISION OF ALTERNATIVE EMISSION CONTROL SYSTEM COSTS FOR A 10 LTD SULFUR PLANT
(Cost Adjusted to June, 1975)

	Total Costs			Differential Over Preceding Case			
Control System	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Unit Cost ($/ton)
Base Case	$ 902,000	$133,600	93	-	-	-	18
Alternative I	1,028,000(a)	198,800(a)	19	126,000	65,200	74	210(b)
Alternative II							
Oxidation	1,320,000(a)	352,200(a)	2	292,000	153,400	17	2148(b)
Reduction	1,765,000(a)	442,000(a)	2	737,000	243,200	17	3406(b)

Notes:
(a) Includes costs of base case Claus sulfur recovery plant.
(b) Incremental costs per incremental ton of SO_2 recovered.

Table 8-10. COMPARISON OF ALTERNATIVE EMISSION CONTROL SYSTEM COSTS FOR A 5 LTD SULFUR PLANT

	Total Costs			Differential Over Preceding Case			
Control System	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Unit Cost ($/ton)
Base Case	$ 757,000	$147,500	46.5	-	-	-	39
Alternative I	847,000(a)	205,900(a)	9.5	$ 90,000	$ 58,400	37.0	375(b)
Alternative II							
Oxidation	1,095,000(a)	344,800(a)	1	248,000	138,900	8.5	3891(b)
Reduction	1,456,000(a)	419,900(a)	1	609,000	214,000	8.5	5994(b)

Note:
(a) Includes costs of base case Claus sulfur recover plant.
(b) Incremental costs per incremental ton of SO_2 recovered.

Table 8-11. LARGE REFINER--DERIVATION OF MODEL FINANCIAL PROFILE[16]

A. Base Financial Data

	Total Company Statistics--Including Foreign Operations: 1972-1974 Average					
	Exxon	Mobile	Shell	Phillips	Cities Service	Ashland
Assets	$25,990	11,327	5,561	3,635	2,654	1,476
Sales	30,618	13,162	6,312	3,494	2,234	2,619
Total Costs of Operations	23,605	10,764	5,739	3,062	2,025	2,473
Profit Before Taxes	7,013	2,398	573	432	209	146
Taxes	4,640	1,575	168	172	55	58
Net Profit	2,373	823	405	260	154	88
Total Petroleum Sales (Barrels/Year)	1,958	816	379	163	89	121[a]

NOTE: All quantities in millions.

B. Financial Profile

	$/Barrel
Assets	14.363
Sales	16.574
Total Cost of Operations	13.519
Profit Before Taxes	3.055
Taxes	1.891
Net Profit	1.164
% Return on Assets	8.10%

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[a] Year ending September 30.

The financial profile of the smaller, less complex firm is based upon an analysis of the published financial statements of Murphy Oil Corporation, Quaker State Oil Refining Corporation, APCO Oil Corporation, United Refining Company, and Edgington Oil Company. These firms considered together should adequately represent the small refiner sector of the domestic oil industry. The resulting financial profile is presented in Table 8-12.

The economic impact associated with standards of performance results from the incremental cost imposed on a source to comply with these standards above those imposed on a source to comply with existing state or local air pollution regulations. As discussed in Chapter 3, most State Implementation Plans to meet the national ambient air quality standards for SO_2 require new plants to achieve an overall sulfur recovery of 99.0 percent. A few local air pollution control regulations require an overall sulfur recovery of 99.9 percent. Consequently, most state or local regulations already require the installation of an alternative I emission control system and standards of performance based on this alternative will have no economic impact.

To assess the economic impact associated with standards based on emission control system alternative II, the effect of compliance with standards on the financial profile of a typical refiner was evaluated. Eleven cases covering various refinery and sulfur plant capacities were examined, three representing a large refiner and eight representing a small refiner. These cases are presented in Tables 8-13 through 8-23 and are summarized in Table 8-24.

Table 8-12. SMALL REFINER--DERIVATION OF MODEL FINANCIAL PROFILE[16]

A. Base Financial Data

Total Company Statistics--Including Foreign Operations: 1972-1974 Average

	Murphy	Quaker State	Apco	United	Edgington
Assets	$771.1	171.1	167.2	83.7	41.8
Sales	592.3	213.7	165.5	165.1	85.6
Total Cost of Operations	506.1	179.6	159.5	155.6	72.6
Profit Before Taxes	86.2	34.1	6.0	9.5	13.0
Taxes	43.3	14.6	2.9	4.7	5.9
Net Profit	42.9	19.5	3.1	4.8	7.1
Total Petroleum Sales (Barrels/Year)	51.0	6.7	19.4	20.1[a]	10.5[a]

NOTE: All quantities in millions.

B. Financial Profile

	$/Barrel
Assets	11.466
Sales	11.348
Total Cost of Operation	9.967
Profit Before Taxes	1.382
Taxes	0.663
Net Profit	0.719
% Return on Assets	6.27%

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[a] Based on 90% of capacity, crude runs not given in Moody's.

Table 8-13. CASE 1: 100 LTD SULFUR PLANT/100,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	14.363	0.029	0.048	0.076	-	0.019	0.047	-	14.382	14.410
Sales	16.574	0.001	0.001	0.001	-	-	-	-	16.574	16.574
Cost of Operation	13.519	0.007	0.016	0.021	-	0.009	0.014	-	13.528	13.533
Profit Before Taxes	3.055								3.046	3.041
Net Profit	1.164								1.161	1.159
% Return on Assets	8.10								8.07	8.04
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.012	0.023
%									0.07	0.14

Notes:
1. All values in dollars per barrel.
2. Larger refiner model financial profile, Table 8-11.
3. Derived from Table 8-8; assumes 350 operating days per year for sulfur plant.

Table 8-14. CASE 2: 100 LTD SULFUR PLANT/50,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	14.363	0.057	0.095	0.152	-	0.038	0.095	-	14.401	14.458
Sales	16.574	0.002	0.002	0.002	-	-	-	-	16.574	16.574
Cost of Operation	13.519	0.016	0.034	0.042	-	0.018	0.026	-	13.537	13.545
Profit Before Taxes	3.055								3.037	3.029
Net Profit	1.164								1.157	1.154
% Return on Assets	8.10								8.03	7.98
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.025	0.045
%									0.15	0.27

Notes:
1. All values in dollars per barrel.
2. Larger refiner model financial profile, Table 8-11.
3. From Table 8-8; assumes 350 operating days per year for sulfur plant.

Table 8-15. CASE 3: 50 LTD SULFUR PLANT/50,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	14.363	0.024	0.035	0.088	-	0.011	0.064	-	14.374	14.427
Sales	16.574	0.001	0.001	0.001	-	-	-	-	16.574	16.574
Cost of Operation	13.519	0.008	0.011	0.025	-	0.003	0.017	-	13.522	13.536
Profit Before Taxes	3.055								3.052	3.038
Net Profit	1.164								1.163	1.157
% Return on Assets	8.10								8.09	8.02
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.004	0.029
%									0.02	0.18

Notes:
1. All values in dollars per barrel.
2. Larger refiner model financial profile, Table
3. Interpolated from Tables 8-8 and 8-9.

Table 8-16. CASE 4: 50 LTD SULFUR PLANT/30,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.040	0.058	0.147	-	0.018	0.107	-	11.484	11.573
Sales	11.348	0.002	0.002	0.002	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.014	0.030	0.042	-	0.016	0.028	-	9.983	9.995
Profit Before Taxes	1.382								1.365	1.353
Net Profit	0.719								0.710	0.704
% Return on Assets	6.27								6.18	6.08
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.019	0.042
%									0.17	0.37

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. Interpolated from Tables 8-8 and 8-9.

Table 8-17. CASE 5: 30 LTD SULFUR PLANT/30,000 BCD REFINERY[1]

	Financial Profile Base Case	Cost of Control			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.026	0.077	0.115	-	0.051	0.089	-	11.517	11.555
Sales	11.348	0.001	0.001	0.001	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.011	0.032	0.038	-	0.021	0.027	-	9.988	9.994
Profit Before Taxes	1.382							-	1.360	1.354
Net Profit	0.719							-	0.708	0.704
% Return on Assets	6.27							-	6.14	6.09
Price Increase Necessary to Maintain Return on Assets										
$/BBL								-	0.028	0.038
%								-	0.24	0.34

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. Interpolated from Tables 8-8 and 8-9.

Table 8-18. CASE 6: 10 LTD SULFUR PLANT/30,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.012	0.038	0.079	-	0.026	0.067	-	11.492	11.533
Sales	11.348	-	-	-	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.006	0.020	0.029	-	0.014	0.023	-	9.981	9.990
Profit Before Taxes	1.382								1.367	1.358
Net Profit	0.719								0.711	0.706
% Return on Assets	6.27								6.19	6.12
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.018	0.033
%									0.16	0.29

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. From Table 8-9.

Table 8-19. CASE 7: 30 LTD SULFUR PLANT/20,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.039	0.115	0.173	-	0.076	0.134	-	11.542	11.600
Sales	11.348	0.001	0.001	0.001	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.016	0.048	0.057	-	0.032	0.041	-	9.999	10.008
Profit Before Taxes	1.382							-	1.349	1.340
Net Profit	0.719							-	0.702	0.697
% Return on Assets	6.27							-	6.08	6.01
Price Increase Necessary to Maintain Return on Assets										
$/BBL								-	0.042	0.058
%								-	0.37	0.51

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. Interpolated from Tables 8-8 and 8-9.

Table 8-20. CASE 8: 10 LTD SULFUR PLANT/20,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.017	0.057	0.118	-	0.040	0.101	-	11.506	11.567
Sales	11.348	-	0.001	0.001	-	0.001	0.001	-	11.349	11.349
Cost of Operation	9.967	0.009	0.030	0.042	-	0.021	0.033	-	9.988	10.000
Profit Before Taxes	1.382								1.361	1.349
Net Profit	0.719								0.708	0.702
% Return on Assets	6.27								6.15	6.07
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.026	0.045
%									0.23	0.40

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. From Table 8-9.

Table 8-21. CASE 9: 5 LTD SULFUR PLANT/20,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.012	0.046	0.096	-	0.034	0.084	-	11.500	11.550
Sales	11.348	-	-	-	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.008	0.027	0.037	-	0.019	0.029	-	9.986	9.996
Profit Before Taxes	1.382								1.362	1.352
Net Profit	0.719								0.709	0.703
% Return on Assets	6.27								6.16	6.09
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.026	0.040
%									0.23	0.35

Notes:
1. All values in dollars per barrel.
2. Smaller refinery model financial profile, Table 8-12.
3. From Table 8-10.

Table 8-22. CASE 10: 5 LTD SULFUR PLANT/15,000 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.016	0.062	0.128	-	0.046	0.112	-	11.512	11.578
Sales	11.348	-	-	-	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.011	0.036	0.050	-	0.025	0.039	-	9.992	10.006
Profit Before Taxes	1.382								1.356	1.342
Net Profit	0.719								0.706	0.698
% Return on Assets	6.27								6.13	6.03
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.031	0.053
%									0.28	0.47

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. From Table 8-10.

Table 8-23. CASE 11: 5 LTD SULFUR PLANT/7500 BCD REFINERY[1]

	Financial Profile Base Case[2]	Cost of Control[3]			Impact of NSPS			NSPS Impact on Financial Profile		
		Alternative I	Alternative II		Alternative I	Alternative II		Alternative I	Alternative II	
			Oxidation	Reduction		Oxidation	Reduction		Oxidation	Reduction
Assets	11.466	0.033	0.123	0.255	-	0.090	0.222	-	11.556	11.688
Sales	11.348	0.001	0.001	0.001	-	-	-	-	11.348	11.348
Cost of Operation	9.967	0.022	0.073	0.100	-	0.051	0.078	-	10.018	10.045
Profit Before Taxes	1.382								1.330	1.303
Net Profit	0.719								0.692	0.678
% Return on Assets	6.27								5.99	5.80
Price Increase Necessary to Maintain Return on Assets										
$/BBL									0.063	0.106
%									0.55	0.93

Notes:
1. All values in dollars per barrel.
2. Smaller refiner model financial profile, Table 8-12.
3. From Table 8-10.

Refinery Capacity (BCD)	Sulfur Plant Capacity (LTD)	Profitability (% Return on Assets)			Price Increase to Maintain Profitability					
		Alternative I	Alternative II		Alternative I		Alternative II			
			Oxidation	Reduction	($/BBL)	(%)	Oxidation		Reduction	
							($/BBL)	(%)	($/BBL)	(%)
Large Refiner	-	8.10			-	-	-	-	-	-
100,000	100	No Impact	0.37	0.74	No Impact		0.012	0.07	0.023	0.14
50,000	100		0.86	1.48			0.025	0.15	0.045	0.27
50,000	50		0.12	0.99			0.004	0.02	0.029	0.18
Small Refiner	-	6.27			-	-	-	-	-	-
30,000	50	No Impact	1.44	3.03	No Impact		0.019	0.17	0.042	0.37
30,000	30		2.07	2.87			0.028	0.24	0.038	0.34
30,000	10		1.28	2.39			0.018	0.16	0.033	0.29
20,000	30		3.03	4.15			0.042	0.37	0.058	0.51
20,000	10		1.91	3.19			0.026	0.23	0.045	0.40
20,000	5		1.75	2.87			0.026	0.23	0.040	0.35
15,000	5		2.23	3.83			0.031	0.28	0.053	0.47
7,500	5		4.45	7.50			0.063	0.55	0.106	0.93

As shown by the large refiner cases of Table 8-24, standards based on emission control system alternative II decrease the profitability (as measured by return on assets) of a large integrated refiner by 0.37 to 1.48 percent, if unaccompanied by price increases. To maintain an 8.10 percent return on assets, a large refiner would have to increase prices for petroleum products by 0.02-0.27 percent, or about 0.4-4.5 cents per barrel. It is highly unlikely that this impact would retard industry growth among the large integrated refiner sector of the domestic petroleum refining industry. The reduced profitability, or the increase in product prices necessary to maintain profitability, are for all practical purposes negligible.

As might be expected, the impact of standards on a small refiner is greater than that on a large refiner due to economies of scale. As shown by the small refiner cases of Table 8-24, standards based on emission control system alternative II decrease the profitability of a small refiner by 1.28 to 7.50 percent, if unaccompanied by price increases. To maintain a 6.27 percent return on assets, the small refiner would have to increase prices for petroleum products by 0.16 to 0.93 percent, or about 1.8 to 10.6 cents per barrel. Although it appears that the impact of standards on the smallest refiner may be from three to five times as severe as that on the typical large refiner, the magnitude of this impact is still quite small and not likely to retard industry growth among the small refiner sector of the domestic petroleum refining industry. As with the large refiner, the price increases necessary to maintain profitability are negligible, especially in light of price increases over the past three to five years.

The impact analysis by refinery size is clouded by the relatively small size of the control investment and annual cost compared with the overall refinery operation. There is, however, a more pronounced effect when the incremental differences between control units is considered. Table 8-25, which is derived from Tables 8-8 - 8-10, presents the incremental costs of achieving alternative II utilizing five sizes of control units. Due to economies of scale, the cost of controlling an incremental ton of SO_2 at the level of alternative II goes from $468-678 for a 100 LTD sulfur plant to $3,891-5,994 for a 5 LTD sulfur plant.

Nation-Wide

Table 8-26 provides the number and size distribution of Claus plant affected facilities in the period 1976-1980. It should be noted that the growth is greater than the projected annual increase of refinery throughput for three reasons. First, approximately 30 percent of the current refining capacity is not controlled by Claus units so the base is narrow. Second, it is assumed that all future refinery capacity will be controlled and third there will be an annual replacement of 5 percent of the existing Claus plants.

Table 8-27 develops the 1976-1980 forecast to show the national impact of required investment dollars, the annual costs and the potential emission reductions. Standards based on alternative I will have no impact. Standards based on alternative II, on the other hand will require an incremental investment by the domestic petroleum refining industry of some $110 MM over the five-year period of 1975 to 1980. In 1980, these standards will increase the annual operating costs of the domestic industry by some $16 MM per year. In return, the standards will reduce national SO_2 emissions by some 57,000 tons per year.

Table 8-25. COST EFFECTIVENESS VS. SIZE OF CONTROL UNIT

	Base Case (Alternative I)		Alternative II	
Sulfur Plant Capacity (LTD)	Emissions Controlled[1] (SO_2, ST/Yr)	Costs[2] (\$/Ton SO_2)	Emissions Controlled[3] (SO_2, ST/Yr)	Costs[4,5] (\$/Ton SO_2)
100	77,615	(0.20)	706	573
50	38,810	1.49	353	736
30	23,285	5.80	212	1,257
10	7,760	25.62	70	2,777
5	3,880	53.07	35	4,943

Notes:

1. 99.0% Sulfur recovery
2. Includes cost of sulfur plant and emission control alternative I
3. Additional emissions controlled at 99.9% sulfur recovery
4. Cost of oxidation and reduction emission control systems averaged
5. Incremental costs per incremental ton of SO_2 controlled

Table 8-26. PROJECTED GROWTH OF REFINERY SULFUR PLANTS 1976-1980[1,2,7]

Claus Plant Size, LTD			Percent of	
Nominal	Range	New Plants	Total Plants	Total Capacity
7.5	5-10	3	3	-
15	10-20	11	10	2
25	20-30	4	4	1
50	30-70	22	21	14
100	>70	67	62	83
	TOTALS	107	100	100

Table 8-27. NATIONAL INVESTMENT, ANNUALIZED COSTS AND EMISSIONS (1980)

Sulfur Plant Capacity (LTD)		Number of Plants	Cost of Control				Impact of NSPS				Emissions			
			Investment[1] (MM$)		Annual Costs[2] (MM$/Yr)		Investment[1] (MM$)		Annual Costs[2] (MM$/Yr)		Emitted[3] (MT/Yr)		NSPS Impact[3] (MT/Yr)	
Nominal	Range		Altn. I	Altn. II[4]	Altn. I	Altn. II[4]	Altn. I	Altn. II	Altn. I	Altn. II	Altn. I	Altn. II	Altn. I	Altn. II
7.5	5-10	3	0.33	1.85	0.20	0.58	-	1.52	-	0.38	0.18	0.02	-	0.16
15	10-20	11	1.87	8.47	0.83	2.38	-	6.60	-	1.55	1.29	0.13	-	1.16
25	20-30	4	1.00	3.68	0.38	1.00	-	2.68	-	0.62	0.78	0.08	-	0.70
50	30-70	22	3.68	27.94	2.98	5.71	-	18.26	-	2.73	8.62	0.86	-	7.76
100	>70	67	70.02	154.64	16.76	27.10	-	84.62	-	10.34	52.53	5.25	-	47.28
	TOTAL	107	82.90	196.58	21.15	36.77	-	113.68	-	15.62	63.40	6.34	-	57.06

Notes
1. Total investment 1975-1980.
2. Fifth year annualized costs (1980).
3. In 1980.
4. Alternative II oxidation and reduction system costs averaged.

8.4 POTENTIAL SOCIO-ECONOMIC AND INFLATIONARY IMPACT

Since the emission control systems required to comply with standards based on either emission control system alternatives represent such a small proportion of the overall equipment or investment required by a petroleum refinery, there should be no more socio-economic impact associated with standards than associated with the addition of any new processing unit to a refinery.

The inflationary impact associated with standards of performance for refinery sulfur plants is negligible. If standards are based on emission control system alternative I, there is no inflationary impact at all. If standards are based on emission control system alternative II, the fifth-year annualized costs are about $16 MM/year, and the price increases necessary to maintain the current industry average return on investment varies from $0.004 to $0.106 per barrel, depending on the size of the refinery affected. These are well below the Environmental Protection Agency's guidelines for preparation of inflationary impact statements.

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9. RATIONALE FOR THE STANDARDS

9.1 SELECTION OF SOURCE FOR CONTROL

Sulfur dioxide emissions from petroleum refineries are a function of the sulfur content of the crude oil processed and the complexity of the refinery itself. A major portion of the sulfur which enters the refinery in the crude oil leaves the refinery in the various petroleum products produced. Most of the sulfur not accounted for in these petroleum products is recovered as elemental sulfur, or emitted to the atmosphere as SO_2.

The major SO_2 emission sources in petroleum refineries are gas and liquid fuel combustion, fluid catalytic cracking unit catalyst regeneration and elemental sulfur recovery. Standards of performance limiting SO_2 emissions from gaseous fuel combustion were promulgated on March 4, 1974 (39 FR 9308). These standards essentially require the removal of H_2S from fuel gas before it is burned, thus forcing increased elemental sulfur recovery within petroleum refineries.

Petroleum refinery sulfur recovery plants, however, as mentioned above, are responsible for a sizeable portion of the total SO_2 emissions emitted from petroleum refineries. In 1975, nationwide refinery sulfur recovery plant SO_2 emissions were estimated to be 0.272×10^6 MT/yr, or about 10% of total domestic refinery SO_2 emissions. Although refinery sulfur recovery plants are responsible for only a small portion (about 1%) of the total unabated U.S. SO_2 emissions, the expected rapid growth of these facilities emphasizes the need for their control. As of April 1975, there were 122 sulfur recovery plants located in 81 domestic refineries. Between 1976 and 1980, 107 new plants are expected to be built. Well over half of these new plants (about 62%) will have an average size of 100 LTD. The total combined capacities of these new plants will be about 6,000 LTD so that by 1980 the number of refinery sulfur recovery plants will double.

A very important consideration of developing standards for refinery sulfur recovery plants is that most refineries are located in or near urban areas. As the size and number of these refineries increase and the average sulfur content of the crude oil processed increases, control of SO_2 emissions becomes much more critical.

9.2 SELECTION OF THE BEST SYSTEM OF EMISSION REDUCTION

As discussed in chapter 6, two alternative emission control systems are considered candidates to serve as the basis for standards of performance (i.e. best system of emission reduction, considering costs). These systems are the third-stage low temperature Claus reactor system (alternative I) and various tail gas scrubbing systems (alternative II).

Considering only the performance of these systems, the alternative II systems are clearly superior to the alternative I systems. (See chapters 4 and 6.) Use of an alternative II emission control system increases the overall sulfur recovery of a refinery sulfur plant from about 95 percent to 99.9 percent, compared to 99 percent with use of an alternative I emission control system. In terms of emission reduction, the alternative II systems reduce emissions by 98-99 percent, compared to an emission reduction of only 80-85 percent achieved by the alternative I systems. Also, the alternative II emission control systems are essentially insensitive to fluctuations which might occur in the composition of the tail gases from the sulfur plant. The alternative I systems, however, require strict maintenance of a 2:1 H_2S/SO_2 ratio to function properly. Thus, the alternative II systems are much less prone to upsets and are able to limit emissions to lower levels over a wider variety of operating conditions than the alternative I systems.

Considering the various environmental impacts associated with both alternatives, the alternative II emission control systems again emerge as clearly superior to those of alternative I. (See chapter 7.) In terms of ambient air quality, although the alternative I emission control systems result in a significant reduction in the maximum ambient air concentrations of SO_2 arising from the operation of a refinery sulfur plant, the alternative II systems result in a substantially greater reduction of these concentrations. More importantly, however, most State implementation plans (SIP) already require a level of control essentially equivalent to the alternative I emission control systems. Consequently, standards based on this alternative would have little or no impact on emissions of SO_2 from new or modified refinery sulfur plants. Standards based on the alternative II systems, however, will reduce these emissions by about 90 percent and will lead to a reduction in the growth of national SO_2 emissions by 1980 of some 55,000 tons per year.

Considering possible environmental impacts in other areas, there are essentially no potential adverse water pollution or solid waste impacts associated with either alternative emission control system. With regard to energy consumption, both alternatives reduce the overall energy consumption associated with a refinery sulfur plant. Since most SIP's already require the installation of alternative I emission control systems, no reduction in energy consumption can be associated with standards based on this alternative. If standards are based on the alternative II systems, however, the growth in national energy consumption will be reduced by some 54 million kw-hr/yr (90,000 barrels of fuel oil per year) by 1980.

With regard to other areas of potential environmental impacts, there appear to be no noise or radiation impacts, or any irreversible or irretrievable commitment of resources associated with either of these alternative emission control systems. Neither does there appear to be any incentive for not developing or delaying standards.

In terms of the economic impacts associated with the alternative emission control systems, the alternative II systems generally cost about twice as much to install and about 2 1/2 times as much to operate as the alternative I systems. Again, however, since most SIP's already require the installation of alternative I emission control systems, there will be no economic impact if standards are based on this alternative. If standards are based on alternative II, the impact on a typical large integrated refinery will reduce its profitability from about 8.10 percent return on assets to about 7.98-8.09 percent. To maintain an 8.10 percent return on assets, the refiner would have to increase prices for petroleum products by only 0.03-0.12 cents per gallon, or less than 0.5 percent. The magnitude of this impact, therefore, is negligible.

The impact on a typical small refinery is larger than that on a large refinery due to the "economies-of-scale". In this case the impact of standards based on the alternative II emission control systems will reduce the profitability of a small refinery from about 6.27 percent return on assets to about 5.80-6.18 percent. To maintain a 6.27 percent return on assets, the small refiner would have to increase prices on petroleum products by about 0.06-0.25 cents per gallon, or 0.16-0.94 percent. While this impact is about twice as severe on the small refiner as on the large refiner, its magnitude is still quite small and not likely to retard growth among the small refiner sector of the domestic refining industry. As with the large refiner, the price increases necessary to maintain profitability are negligible, certainly in light of price increases over the past three to five years.

In terms of the national impact on the domestic petroleum refining industry, standards based on the alternative I emission control systems will have no impact. Standards based on the alternative II systems, however, will increase the national investment required by the domestic industry by some $115 MM over the five-year period from 1975 to 1980; and the annual operating costs of the industry will be increased by some $16 MM per year in 1980.

The potential inflationary impact of these standards is essentially negligible. If standards are based on the alternative I emission control systems, there is no impact, and if standards are based on the alternative II systems, the increased fifth-year annualized costs and increased product prices are well below the

Agency's guidelines of $100 MM per year and 5 percent for signalling potential inflationary impact.

It is clear, therefore, that the alternative II emission control systems must be selected as the "best system of emission reduction, considering costs" and that standards of performance for refinery sulfur plants must be based on the use of these systems.

9.3 SELECTION OF POLLUTANTS FOR CONTROL

As discussed above, sulfur recovery plants in petroleum refineries are major point sources of SO_2 emissions. The objective of standards of performance, therefore, is to reduce these emissions from new and modified refinery sulfur plants. Selecting emission control system alternative II as the basis for standards, however, complicates the selection of pollutants for control.

Emission control system alternative II refers to two different processes: oxidation-scrubbing and reduction-scrubbing. Residual emissions released to the atmosphere from oxidation-scrubbing processes consist of SO_2. Residual emissions released to the atmosphere from reduction-scrubbing processes, however, consist of SO_2 if the tail gases are incinerated before release to the atmosphere, or a mixture of reduced sulfur compounds such as hydrogen sulfide (H_2S), carbonyl sulfide (COS) and carbon disulfide (CS_2), if the tail gases are not incinerated (see chapters 4 and 6). A limit on SO_2 emissions alone, therefore, while appropriate for the oxidation-scrubbing processes, and those reduction-scrubbing processes with tail gas incineration, is inappropriate for those reduction-scrubbing processes without tail gas incineration.

While emissions of H_2S from the reduction-scrubbing processes without tail gas incineration can vary widely depending on the design and operation of the process, emissions of COS and CS_2 will not exceed 90-100 ppm unless the reduction catalyst in the process is permitted to deteriorate. Consequently, the major potential air pollution problem posed by these processes is emissions of H_2S.

Minimizing emissions of H_2S from reduction-scrubbing processes without tail gas incineration requires design and operation of the scrubbing portion of the process to reduce emissions of H_2S to very low levels initially. If standards of performance do not limit emissions of H_2S, owners or operators of these processes could operate only the reduction portion of these systems and by-pass the scrubber portion. The SO_2 originally present would merely be converted to H_2S and released directly to the atmosphere. Although this is possible, it is unlikely because at the ambient air concentration of H_2S which would result (500-2000 $\mu g/m^3$, with short-term peaks, 2-10 second, approaching 25,000 $\mu g/m^3$) an extremely severe odor problem would result (see chapter 7). Sources would tend to control these H_2S emissions to very low levels due to the offensive odors which would otherwise result if they were not controlled.

Even in the more likely situation, however, where emissions of H_2S were reduced to the range of 200-300 ppm before release to the atmosphere, ambient air concentrations of H_2S ranging from 15 to 60 $\mu g/m^3$ could arise with short-term peaks as high as 500 to 800 $\mu g/m^3$. Since the odor threshold for H_2S is 45 $\mu g/m^3$, an odor air pollution problem could still arise.

Although emissions of COS and CS_2 are normally very low, as mentioned above, if the reduction catalyst is permitted to deteriorate, emissions of these compounds from reduction-scrubbing processes without tail gas incineration can approach 1000 ppm. Under these conditions, ambient air concentrations of COS and CS_2 ranging from 100 to 400 $\mu g/m^3$ could arise, with short-term peaks approaching 3500 to 5500 $\mu g/m^3$, respectively. While ambient air concentrations of COS and CS_2 at these levels probably do not pose health problems, so little health effects data is available on COS and CS_2 that this is questionable. (The little data available indicate adverse health effects occurring only at levels greater than 15,000 $\mu g/m^3$ for CS_2, with no data available for COS--see chapter 7.) The data do indicate, however, that these short-term peak ambient air concentrations of CS_2 are at the odor threshold level for CS_2, so that transitory odors could also arise if the reduction catalyst is permitted to deteriorate.

Developing standards of performance to limit emissions of SO_2 from refinery sulfur recovery plants, therefore, gives rise to a rather unusual situation. In some cases, compliance with these standards, while eliminating SO_2 emissions, would lead to emissions of reduced sulfur compounds (i.e. H_2S, COS and CS_2), which could lead to an odor air pollution problem. Consequently, two alternative courses of action emerge with regard to selecting the pollutants for control by standards of performance for refinery sulfur recovery plants:

1. Limit emissions of SO_2 only
2. Limit emissions of both SO_2 and reduced sulfur compounds

Limiting emissions of reduced sulfur compounds (i.e. H_2S, COS and CS_2) from reduction-scrubbing emission control systems without tail gas incineration, however, would make these pollutants "designated pollutants," and all existing reduction-scrubbing emission control systems without tail gas incineration installed on refinery sulfur recovery plants "designated facilities," under section 111(d) of the Clean Air Act. EPA's regulations implementing section 111(d) (40 CFR §60) would require the Agency to issue a draft guideline document containing the necessary information for states to develop plans for controlling these pollutants from these existing facilities and to solicit public comments on this document. Following consideration of these comments, the Agency would make appropriate changes to the guideline document and issue it in final form. Those states containing reduction-scrubbing emission control systems without tail gas incineration installed on refinery sulfur plants would then be required to develop plans for controlling emissions of these pollutants from these facilities with public hearings to solicit the views of interested parties. These plans would then be submitted to the Agency for approval or disapproval. If a State's plan were disapproved, the Agency would have to develop a plan for that state.

Currently, there are about 25 reduction-scrubbing emission control systems without tail gas incineration now operating on petroleum refinery sulfur recovery plants in some seven states. Developing State plans to limit emissions of reduced sulfur compounds from these facilities, therefore, could be a significant undertaking requiring the expenditure of considerable resources at the Federal, State and local level.

Emissions of reduced sulfur compounds from these existing reduction-scrubbing emission control systems without tail gas incineration, however, are quite low. These systems have been installed to comply with State or local air pollution regulations limiting emissions of SO_2 from existing refinery sulfur recovery plants. To ensure that the installation of these emission control systems do not lead to local odor problems, these regulations also limit emissions of H_2S, COS and CS_2, either directly or indirectly. Where emissions of reduced sulfur compounds are limited directly, local regulations specify the maximum concentrations of H_2S, COS and CS_2 that can be present in the tail gases discharged to the atmosphere. In each case where this approach has been followed, emissions of H_2S are limited to 10 ppm and emissions of total sulfur (H_2S, COS and CS_2) are limited to either 300 or 500 ppm.

Where emissions of reduced sulfur compounds are limited indirectly by local regulations, these regulations require that the best available emission control technology be installed. In the process of specifying what the best emission control technology is, local air pollution control agencies generally contact EPA, vendors of various emission control systems and other local air pollution control agencies where various emission control systems have been installed.

In terms of emissions of reduced sulfur compounds from existing reduction-scrubbing emission control systems without tail gas incineration, this approach has achieved the same end result as that above, and all 25 of these systems which are now operating have been designed and guaranteed by the vendors of these systems to limit emissions to less than 10 ppm H_2S and less than 300 or 500 ppm total sulfur (H_2S, COS and CS_2).[1]

Consequently, existing reduction-scrubbing emission control systems without tail gas incineration are not considered significant sources of reduced sulfur compound emissions. Developing State regulations to control emissions of these pollutants from these facilities, therefore, would accomplish no additional reduction in reduced sulfur compound emissions.

Probably the major reason why existing reduction-scrubbing emission control systems without tail gas incineration are not sources of reduced sulfur compound emissions is that to date, these systems have only been installed in heavily industrialized metropolitan areas. In these areas, the need for air pollution control is generally well recognized and the local air pollution control agencies have been in a position to develop and enforce strong air pollution regulations.

Standards of performance for refinery sulfur plants, however, will require the installation of oxidation-scrubbing or reduction-scrubbing emission control systems on new or modified refinery sulfur recovery plants throughout the United States. In some areas where these systems might be installed, the need for stringent air pollution control might not be as great as it is in these areas where these systems have already been installed. In these areas, owners and operators who installed a reduction-scrubbing emission control system without tail gas incineration would not face stringent regulation of reduced sulfur compounds and they might permit emissions of H_2S to increase to the range of 200 to 300 ppm. At this point the resulting ambient air concentrations of H_2S would lead to noticeable but intermittent and transitory odors as discussed earlier. It is quite possible, therefore, that in complying with standards of performance, some new refinery sulfur plants could become sources of emissions of reduced sulfur compounds unless the standards specifically limit emissions of these pollutants.

Preventing new air pollution problems from arising, however, is one of the primary goals of standards of performance. Also, standards of performance are to reflect the best systems of emission reduction, taking into account the costs of installing and operating these systems. Considered from this perspective, since the technology for reducing emissions of reduced sulfur compounds from reduction-scrubbing systems without tail gas incineration is well demonstrated, the costs of controlling these emissions are reasonable, and not controlling these emissions could lead to an adverse environmental impact in some cases; reduction-scrubbing emission control systems without tail gas incineration can only be included among the best systems of emission reduction if emissions of reduced sulfur compounds are controlled.

It is also through standards of performance that the Agency identifies the best systems of emission reduction for various industrial sources of air pollution. If the Agency were not to limit emissions of reduced sulfur compounds, therefore, it would imply that the Agency does not consider controlling these emissions from reduction-scrubbing processes necessary. This view could serve to undercut or weaken those local air pollution regulations which are now effectively controlling these emissions from existing sulfur recovery plants which have installed reduction-scrubbing emission control systems without tail gas incineration.

A number of good reasons exist, therefore, for extending the standards to cover emissions of reduced sulfur compounds. However, a problem may arise if the burden of the state plan submission required by 40 CFR §60.23 outweighs its possible benefits. To resolve this problem, it is appropriate to consider the intent of both standards of performance and section 111(d).

Briefly, the intent of standards of performance is to require the installation of the best systems of emission control at the time a source is being constructed or modified. The intent of section 111(d) is to reduce emissions of pollutants emitted from existing facilities which pose a danger to the public health or welfare, but which on the basis of the information available cannot be controlled under sections 108, 109 and 110 of the Act as criteria pollutants, and which cannot be controlled under section 112 of the Act as hazardous pollutants.

Where an emission control system installed to comply with a standard of performance might lead to the emission of a pollutant not originally emitted by a source, the logical course of action is to limit emissions of this new pollutant to ensure that it does not lead to a new air pollution problem. In cases where the new pollutant is a non-criteria pollutant, it must be decided whether or not to initiate the chain of events leading to the development of state regulations for limiting emissions of this pollutant from existing sources already well controlled for this pollutant.

The pollutants selected for control by these standards, therefore, are SO_2 and reduced sulfur compounds. A determination of the effort involved in developing state plans will enable EPA to determine whether or not to develop a guideline document or initiate the chain of events leading to the development of state plans for controlling emissions of reduced sulfur compounds from existing reduction-scrubbing emission control systems without tail gas incineration which have been installed on refinery sulfur plants.

9.4 SELECTION OF FORMAT FOR THE STANDARDS

A number of different formats could be selected to limit emissions from refinery sulfur plants. Mass standards limiting emissions in terms of overall sulfur recovery (i.e. emissions per unit of sulfur produced or contained in the feed to the plant), or concentration standards limiting the concentration of emissions in the stack gases discharged into the atmosphere, could be developed.

While mass standards may appear more meaningful in the sense that they relate directly to the quantity of emissions discharged into the atmosphere, enforcement of mass standards is more costly and the results more subject to error than enforcement of concentration standards. Determining mass emissions, for example, invariably requires developing a material balance of some form and this requires process data concerning the operation of the plant, whether it be input material flow rates or production flow rates. Gathering this data increases the testing or monitoring necessary and consequently increases the costs. Manipulation of this data increases the number of calculations necessary, compounding the error inherent within the data and increasing the chance for human error.

Enforcement of concentration standards, however, requires a minimum of data and information, decreasing the costs and minimizing the chances for error in determining compliance. Concentration standards are also somewhat more consistent with the concept of basing standards of the "best systems of emission reduction," since vendors of emission control equipment normally guarantee the performance of their equipment in terms of the concentration of emissions discharged.

The primary disadvantage normally associated with concentration standards is that of possible circumvention by dilution of the gases discharged to the atmosphere lowering the concentration of emissions, but not reducing the total mass emitted. To ensure that compliance with concentration standards is not achieved by dilution, however, section 60.12 of 40 CFR Part 60 specifically prohibits the use of dilution as a means of complying with concentration standards.

Consequently, considered primarily from the perspective of enforcement, concentration standards are selected as the format for standards of performance for refinery sulfur plants. The lower resource requirements of concentration standards over mass standards far outweigh their drawbacks.

9.5 SELECTION OF EMISSION LIMITS IN THE STANDARDS

Specific emission limits need to be selected to limit emissions of SO_2 from refinery sulfur plants which employ either oxidation-scrubbing emission control systems or reduction-scrubbing emission control systems with tail gas incineration. Emission limits also need to be selected to limit emissions of H_2S and reduced sulfur compounds (H_2S, COS and CS_2) from refinery sulfur plants which employ reduction-scrubbing emission control systems without tail gas incineration.

The data and information to support selection of these emission limits is summarized in chapter 4 and consists primarily of emission source tests by the Agency or local air pollution control agencies. Since the amount of emission data available is quite limited, a number of factors need to be considered in selecting the specific emission limits.

Considering first the limit for SO_2 emissions, the emission source test data from oxidation-scrubbing emission control systems shows emissions in the range of 10-50 ppm (tests A_1, A_2, A_3, Figure 4-10). These data, however, were collected from a unit operating at less than half its design capacity immediately following a **major** equipment turnaround. Consequently, the data do not reflect emission levels that could be maintained by a unit operating at full capacity over a period of time. According to both vendors and owners and operators, unavoidable equipment deterioration and chemical aging will lead to lower efficiency. Generally, these systems operate for about a year between major equipment turnarounds and during this time, emissions increase by as much as 100 to 200 ppm. Basing the emission limit solely on the basis of this emission data, therefore, would significantly shorten the normal run length between major turnarounds and increase maintenance and chemical replacement costs considerably.

The emission source test data available from reduction-scrubbing emission control systems with tail gas incineration shows emissions of about 200 ppm SO_2 (test C, Figure 4-10). Although this data is not EPA data, but is data from a test by a local control agency (EPA's source testing at this facility was invalidated due to operating problems), the source testing method employed by this local agency is considered comparable to EPA's.

This emission level, however, is considered higher than normal for a typical reduction-scrubbing emission control system with tail gas incineration. According to the operators at this source, this particular facility is significantly under-designed and, in fact, shortly after this emission test data was gathered, it was "de-bottle-necked" and expanded to improve its performance.

In EPA's discussions with the vendors of this facility, they agreed with the operators that it was "under-designed." They also indicated, however, that emissions from typical reduction-scrubbing emission control systems with tail gas incineration are normally comparable to those from oxidation-scrubbing emission control systems, and that emissions from both systems increase to about the same extent between turnarounds due to unavoidable equipment deterioration and chemical aging.

As pointed out in chapters 4 and 7, the reduction-scrubbing emission control systems with tail gas incineration (as opposed to those without tail gas incineration) have a number of advantages over oxidation-scrubbing emission control systems. Operation of these systems involves techniques with which most refiners have had a great deal of experience and thus refiners understand these systems better, tend to experience fewer problems with them and generally tend to favor these systems. More importantly, however, these reduction-scrubbing emission control systems with tail gas incineration produce no wastewater streams that require disposal. Both the oxidation-scrubbing systems and the reduction-scrubbing systems without tail gas incineration generate a wastewater stream.

Considering all these factors, the emission limit for SO_2 emissions is set at 250 ppm. This limit applies to both the oxidation-scrubbing emission control systems and to the reduction-scrubbing emission control systems with tail gas incineration. In view of the limited emission data available and the comments of both the owners and operators and the control system vendors, this appears to be a reasonable emission limit consistent with the performance of these emission control systems. This limit will also ensure that these alternative II emission control systems are installed and well operated.

Considering the emission limit for emissions of H_2S and reduced sulfur compounds, the available emission source testing data from reduction-scrubbing emission control systems without tail gas incineration shows that emissions of these pollutants from these systems are quite low. Emissions of H_2S, for example, were frequently not detectable (tests B_1, B_2, E_1 and F_1, Figure 4-11). In the one test in which emissions of H_2S were detected (test B_2), an analytical method different from that employed by the Agency was used and simultaneous testing by the Agency detected no emissions (test B_3). Review of both the Agency's test method and this other test method indicated that this method which detected H_2S emissions was not as selective as the Agency's in identifying H_2S, and was including some of the COS and CS_2 present as H_2S.

The emission source test data available on emissions of reduced sulfur compounds (H_2S, COS and CS_2) from these emission control systems shows that emissions of these pollutants are in the range of 10-20 ppm (tests B_1, $B2_1$, B_3, E_1 and F_1, Figure 4-12). Here again, however, this data was collected from these systems shortly after major equipment turnarounds, or when they were operating well below their design capacity (as low as 1/3 of design capacity in one case).

Discussions with the vendors of these control systems also indicated that unavoidable equipment deterioration and chemical aging leads to a gradual increase in emissions with time. Pilot plant data, for example, indicates that emissions increase by about 200 ppm over a year's operation. Thus, as discussed above for the oxidation-scrubbing systems and the reduction-scrubbing systems with tail gas incineration, basing the emission limits for reduction-scrubbing emission control systems without tail gas incineration solely on the emission data available would significantly shorten the normal run length between major turnarounds and increase the costs of maintenance and chemical replacement considerably.

Considering these factors, the limit on emissions of H_2S and reduced sulfur compounds from reduction scrubbing emission control systems without tail gas incineration is set at 10 ppm and 300 ppm respectively. The 10 ppm limit on H_2S emissions will ensure that installation of these emission control systems will not lead to a local odor air pollution problem. The 300 ppm limit is equivalent to the 250 ppm limit on SO_2 emissions in the sense that both limits reduce sulfur emissions--be they SO_2 or H_2S, COS and CS_2--to the same level. (The 250 ppm SO_2 limit reflects the larger volume of gases discharged to the atmosphere.)

9.6 SELECTION OF MONITORING REQUIREMENTS AND PERFORMANCE TEST METHODS

The objective of monitoring requirements is to provide a quick and easy means for enforcement personnel to ensure that an emission control system installed to comply with standards of performance is properly operated and maintained. For refinery sulfur recovery plants, the most straightforward means of ensuring proper operation and maintenance is to monitor emissions released to the atmosphere. Consequently, where oxidation-scrubbing processes or reduction-scrubbing processes with tail gas incineration are installed to comply with the standards, monitoring of SO_2 emissions is required. Where reduction-scrubbing processes without tail gas incineration are installed, monitoring of H_2S and reduced sulfur compound emissions is required.

Although monitoring requirements are included for H_2S and reduced sulfur compound emissions, the Agency has not yet developed performance specifications for these monitors. Consequently, owners and operators of reduction-scrubbing emission control systems without tail gas incineration, who are subject to these requirements, will not have to install these monitors until these specifications have been promulgated in the Federal Register. The requirement for monitoring is included in the regulations to ensure that when these monitors become available, sources which became subject to standards of performance before the monitors were available will then be required to install monitors to aid enforcement personnel in determining if the emission control system is being properly operated and maintained.

For determining compliance with the standards, Method 6 - Determination of Sulfur Dioxide Emissions from Stationary Sources will be used where oxidation-scrubbing processes or reduction-scrubbing processes with tail gas incineration are installed. Where reduction-scrubbing processes without tail gas incineration are installed, Method 18 - Determination of Hydrogen Sulfide, Carbonyl Sulfide and Carbon Disulfide Emissions from Stationary Sources will be used. These methods were the methods used to gather the emission data contained in chapter 4 and Appendix C, which support the standards. Details as to why these methods were selected over other methods for gathering this data may be found in Appendix D.

9.7 REFERENCES

1. Telephone conversation, F.L. Porter (EPA) with G.L. Tilley (Union Oil), April 28, 1976.

APPENDIX A

EVOLUTION OF STANDARDS

EVOLUTION OF STANDARDS

Date	
8/73-1/74	Surveyed and reviewed process operations and emission control systems for all domestic Claus sulfur recovery plants.
8/73	Sent letters to control equipment vendors requesting design data for the Wellman-Lord, Beavon, Cleanair, SCOT, and Aquaclaus processes, and location of well-controlled Claus plants.
9/73	Selected eight refineries for initial plant inspections.
10/5/73	Contracted for detailed engineering study of Claus tail gas control systems with Battelle-Columbus.
10/10-10/19/73	Inspected eight refineries with well-controlled Claus plants, pre-surveyed for emission testing, and sent 114 letters to refineries.
10/17/73	Met with Los Angeles APCD for discussion of their regulations for sulfur recovery plants.
11/73	Contractor sent additional letters to vendors for design data on the IFP-1, IFP-2, Sulfreen, Cataban, and Chiyoda Thoroughbred processes for tail gas sulfur removal.
10/73-2/74	Test methods for determining gaseous sulfur compounds in Claus tail gas (i.e., COS, CS_2, H_2S, SO_2, S_x) investigated and developed. Presurveys made of three likely test sites.
1/11/74	Inspection made of IFP-1 process on a Claus sulfur plant.
2/25-3/13/74	Emission tests completed for Wellman-Lord, Beavon, and SCOT control systems.

4/1/74	Inspection made of second IFP-1 process on a Claus sulfur plant. 114 letters on IFP-1 process sent to operators.
5/7/74	Meeting with API's Committee on Environmental Affairs to discuss emission test results and potential standards.
6/10-6/12/74	Emission test of IFP-1 control system completed.
6/74	Study entitled "Characterization of Sulfur Recovery From Refinery Fuel Gas" completed by Battelle-Columbus Labs. Report circulated to API for review.
8/74- 2/75	Emission control costs developed, monitoring and emission test methods finalized, and dispersion analyses completed. Developed first draft of EPA Standards Support and Environmental Impact Document (SSEID).
3/75	Revised SSEID and sent to NAPCTAC and Working Group members.
4/29/75	Met with EPA Working Group to discuss findings of SSEID and the recommended standard.
5/5-5/6/75	Met with NAPCTAC to review the recommended standard for refinery sulfur plants and the basis for the standard outlined in the SSEID.
5-7/75	Delayed action to resolve potential 111(d) aspects of standards for refinery sulfur plants.
8-9/75	Responsibility for SSEID informally transferred to Standards Development Branch.
10/75-4/76	SSEID reviewed, edited and rewritten by Standards Development Branch to conform with the general outline for a SSEID.

APPENDIX B

INDEX TO ENVIRONMENTAL IMPACT CONSIDERATIONS

APPENDIX B

INDEX TO ENVIRONMENTAL IMPACT CONSIDERATIONS

Agency Guidelines for Preparing Regulatory Action Environmental Impact Statements (39 FR 37419)	Location Within the Standards Support and Environmental Impact Statement
1. Background and Description of Proposed Action	
Summary of Proposed Standards	The standards are summarized in chapter 1, section 1.1.
Statutory Basis for the Standard	The statutory basis for the standard is given in chapter 2.
Facility Affected	A description of the facility to be affected is given in chapter 3.
Process Affected	A description of the process to be affected is given in chapter 3.
Availability of Control Technology	Information on the availability of control technology is given in chapter 4.
Existing Regulations at State or Local Level	A discussion of existing regulations on the industry to be affected by the standards is included in chapter 3, section 3.
2. Alternatives to the Proposed Action	
No Action or Postponing Action	
Environmental Impacts	Environmental effects of not implementing the standards are discussed in chapters 3 and 7.
Costs	The costs of not implementing the standards are considered in chapter 8, section 8.1.

INDEX TO ENVIRONMENTAL IMPACT CONSIDERATIONS (continued)

Agency Guidelines for Preparing Regulatory Action Environmental Impact Statements (39 FR 37419)	Location Within the Standards Support and Environmental Impact Statement
Health and Welfare Impact	The health/welfare impact of not implementing the standards is considered in chapter 7.
Alternative I - 99% Control	
Environmental Impacts	The environmental impacts associated with alternative I emission control systems are considered in chapter 7.
Costs	The cost impact of alternative I emission control systems is considered in chapter 8, section 8.2.
Health and Welfare Impact	The impact of alternative I emission control systems on health and welfare is considered in chapter 7.
3. Environmental Impact of Proposed Action	
Air Pollution	The air pollution impact of the standards is considered in chapter 7, section 7.1.
Water Pollution	The impact of the standards on water pollution is considered in chapter 7, section 7.2.
Solid Waste Disposal	The impact of the standard on solid waste disposal is considered in chapter 7, section 7.3.
Energy	The impact of the standards on energy use is considered in chapter 7, section 7.4.

APPENDIX C

EMISSION SOURCE TEST DATA

EMISSION SOURCE TEST DATA

C.1 INTRODUCTION

This appendix summarizes the emission test data gathered during the development of standards for refinery sulfur plants. Detailed information on each facility tested is presented herein. Each facility is identified by the same coding used in Chapter 4. Any reference in this appendix to commercial products or processes by name does not constitute an endorsement by the Environmental Protection Agency.

C.2 SUMMARY OF TEST DATA

Four different processes for removing sulfur from Claus sulfur plant exhaust gases were tested by EPA to determine the best available control technology as required by section 111 of the Clean Air Act. Pollutants measured included total sulfur by EPA Method 18 (gas chromatograph/flame photometric detection), SO_2 by EPA Method 6, H_2S by EPA Method 11, carbon monoxide by EPA Method 10, NO_x by EPA Method 7, hydrocarbons by a flame ionization detector, Orsat gases by EPA Method 3, and moisture by EPA Method 4.

C.3 DESCRIPTION OF FACILITIES

Plant A - Plant A consists of three identical 150 long ton/day (LT/D) Claus trains, two of which operate with the third on stand-by. Emissions from each Claus train is controlled by a Wellman-Lord scrubber. Design basis of these Wellman-Lord scrubbers is 250 ppmv SO_2. Tests A1 and A2 were performed by EPA and refinery personnel, respectively, during the period March 11-13, 1974. In Test A1 sulfur compounds were determined by EPA Method 18 (gas chromatograph/flame photometric detection) for total sulfur and EPA Method 6 for SO_2.

Carbon dioxide, carbon monoxide, and oxygen were determined by continuous methods (non-dispersive infrared for CO_2 and CO and paramagnetic for O_2) and by the Orsat method. Nitrogen oxides were determined by EPA Method 7, visible emissions by EPA Method 9, moisture and flow rates by EPA Methods 1, 2, and 4, and hydrocarbon concentrations by a flame ionization detector.

In Test A2 SO_2 and NO_x were determined by a fuel cell electrochemical method, COS and CS_2 by a gas chromatograph flame photometric detector, CO and CO_2 by Orsat, O_2 by Orsat and a paramagnetic oxygen analyzer, and hydrocarbons by a hydrogen flame gas chromatograph.

During Tests A1 and A2 only one sulfur plant was operating due to low refinery throughputs caused by the OPEC oil embargo. Sulfur feed rates during the tests averaged 113 LT/D for three runs.

Test A3 was conducted by the Los Angeles APCD, January 10-11, 1973, on all three Claus plants. Hydrogen sulfide was determined by a $ZnCO_3$ impinger train, and SO_2 by impingers containing a 5% NaOH solution. Nitrogen oxides, hydrocarbons, carbon monoxide, carbon dioxide, moisture, and flow rates were determined according to methods described in the Source Testing Manual of the Los Angeles APCD.

Sulfur feed to the three plants during Test A3 was 116.6, 76.9, and 68.8 LT/D, respectively, averaging well below design rates.

Plant B - Plant B consists of two parallel 100 LT/D Claus trains, each of which exhausts into a Beavon tail gas treating unit. Design basis of each Beavon tail gas treating unit is 200 ppmv total sulfur, with less than 10 ppmv H_2S.

Tests B1 and B2 were performed by EPA and refinery personnel, respectively, during the period March 5-7, 1974. In Test B1 sulfur compounds were determined by EPA Method 18 (gas chromatograph/flame photometric detection) for total sulfur and EPA Method 6 for SO_2. Carbon dioxide, carbon monoxide, and oxygen were determined by continuous methods (a non-dispersive infrared instrument for CO_2 and CO, and paramagnetic analyzer for O_2) and by the Orsat method. Nitrogen oxides were determined by EPA Method 7, visible emissions by EPA Method 9, moisture and flow rates by EPA Methods 1, 2, and 4, and hydrocarbon concentrations by a flame ionization detector.

In Test B2 mass spectrometry was used to determine CH_4, COS, SO_2, H_2S, CS_2, H_2, CO/N_2, O_2, Ar, and CO_2. Gas chromatography was then used to obtain the CO/N_2 split.

During Tests B1 and B2 the sulfur plants were operating well below design levels due to the OPEC oil embargo. Sulfur feed rate to each or both Claus train(s) averaged 34.2 LT/D for three runs.

Test B3 was conducted by the Los Angeles APCD on three separate occasions: July 10, August 8, and September 24, 1974. The August 8 and September 24 tests were performed before and after overhaul to determine the effect of overhaul on emissions.

Sampling techniques included a 5% HCl solution in an impinger to collect ammonia, a 3% H_2O_2 solution in an impinger to collect SO_2, and a $ZnCO_3$ slurry in an impinger for H_2S collection. Grab samples were made for subsequent determinations of H_2S, COS, and CS_2 by gas chromatograph with a flame photometric detector and carbon monoxide by non-dispersive infrared absorption.

Plant C - Plant C consists of one small 16 LT/D, two-stage Claus unit followed by a SCOT tail gas treating unit. Design basis of the SCOT unit is 400 ppmv total sulfur emissions calculated as H_2S. An incinerator oxidizes the 400 ppm H_2S to SO_2 before discharge to the atmosphere.

Test C3 was conducted by the Los Angeles APCD on February 14, 1974. Hydrogen sulfide was determined by a $ZnCO_3$ train at the outlet of the SCOT system. At the incinerator stack SO_2 was determined by an NaOH train; combustion gases (CO, CO_2, and CH_4) were analyzed by total combustion analysis using a non-dispersive infrared instrument and NO_x was determined by hydrogen peroxide/sulfuric acid impinger trains. Water vapor, gas flow and Orsat gases were also analyzed using Los Angeles APCD methods.

During Test C3 sulfur feed averaged 11.1 LT/D.

Plant D - Test D1 was conducted June 10-12, 1974, by EPA on a large, 395 LT/D, three-stage Claus plant followed by an IFP-1 tail gas process. The Claus plant recovers sulfur from acid gases produced in a carbon disulfide plant. Emission design for the IFP-1 unit is 90 percent conversion of (H_2S + SO_2) from the Claus plant. This corresponds to 1640 ppmv total sulfur (wet) or 2540 ppmv total sulfur (dry).

In the first test total sulfur compounds were determined by EPA Method 18 (gas chromatograph/flame photometric detection). SO_2 was determined by EPA Method 6, H_2S by EPA Method 11, NO_x by EPA Method 7, moisture by EPA Method 4, gas flow by EPA Methods 1 and 2, and visible emissions by EPA Method 9. CO_2, CO and O_2 were determined by continuous methods (non-dispersive infrared for CO_2 and CO, paramagnetic analyzer for O_2). CO_2 and O_2 were also determined by a gas chromatograph with thermal conductivity detection.

The second test was conducted using a Meloy Analyzer, which oxidizes all sulfur compounds to SO_2 and then measures SO_2 by a flame photometric detector. The third test was conducted using a DuPont analyzer, which also oxidizes all sulfur compounds to SO_2, but which then measures SO_2 by UV absorption.

During these tests, sulfur feed to the Claus unit averaged 336 LT/D.

Plant E - Plant E consists of two 96 LT/D Claus plants each with a Beavon tail gas treating unit. Test E1 was conducted December 12, 1974, by the Los Angeles APCD. Analyses for COS, CS_2, H_2S, SO_2, H_2SO_4, total sulfur, CO, and NO_x were conducted. Details on test methodology were not specified, though assumed the same as in previous tests conducted by Los Angeles County (Tests A3 and B3). No process data were available. The Beavon units were designed at 200 ppmv total sulfur, 10 ppmv H_2S emission levels.

Plant F - Plant F consists of a Beavon tail gas treating unit which removes sulfur from four combined Claus plant tail gas streams in a petroleum refinery. No design or operating data are available. Los Angeles County conducted tests November 6, 1974, for total sulfur, H_2S, and carbon monoxide (test F1). Again, test methods are assumed to be Los Angeles APCD methods as described for Tests A3 and B3.

Table 1

FACILITY A
Summary of Results

Test Number		A1		
Run Number	1	2	3	Average
Date	3/11/74	3/12/74	3/13/74	
Stack Effluent:				
Flow rate - DNM^3/min	197.1	135.4	209.7	180.4
Water vapor - Vol. %	13.0	10.6	11.2	11.6
CO_2 - Vol. % dry[a]	-	7.2	5.35	6.3
O_2 - Vol. % dry[a]	-	0.8	2.95	1.9
CO - Vol. % dry[a]	-	0.0	0.0	0.0
CO_2 - Vol. % dry[b]	4.3	5.6	3.8	4.6
O_2 - Vol. % dry[b]	0.9	0.2	1.5	0.9
CO - ppmv dry[b]	95	100	39	78
SO_2 - ppmv dry[c]	5.9	21.8	7.4	11.7
SO_2 - ppmv dry[d]	38	16	10	21
COS - ppmv dry[d]	3.2	1.9	0.9	2.0
CS_2 - ppmv dry[d]	2.5	3.4	1.1	2.3
H_2S - ppmv dry[d]	<0.1	<0.1	<0.1	<0.1
TS - ppmv dry[d]	46.2	24.7	13.1	28
NO_x - ppmv dry[e]	17.2	9.0	21.0	15.7
THC - ppmv dry[f]	7.5	6.2	4.6	6.1
Visible emissions[g]	0	0	0	0

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[a] Orsat analysis

[b] NDIR/Paramagnetic

[c] EPA-6

[d] GC/FPD (EPA-18)

[e] EPA-7

[f] Total hydrocarbons as methane by flame ionization

[g] EPA-9

Source: Reference 1

TABLE 2

FACILITY A

Summary of Results

Test Number		A2	
Run Number	1	2	Average
Date	3/12/74	3/13/74	
Stack Effluent:			
Flow rate DNM^3/MIN	-	-	-
Water vapor - vol. %	-	-	-
CO_2 - vol. % dry[a]	6.6	-	6.6
O_2 - vol. % dry[a]	1.3	-	1.3
CO - vol. % dry[a]	0.3	-	0.3
SO_2 - ppmv dry[b]	10	15	12.5
COS - ppmv dry[c]	0.3	-	0.3
CS_2 - ppmv dry[c]	1.5	-	1.5
NO_x - ppmv dry[b]	21.7	25	23.4
HC - ppmv dry[d]	3.0	-	3.0

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[a] Orsat analysis

[b] fuel cell electrochemical

[c] GC/FPD (EPA-18)

[d] Hydrogen flame chromatography

Source: Reference 2

TABLE 3

FACILITY A
Summary of Results

Test Number	A3			
Run Number	1	2	3	Average
Date	1/10/73	1/11/73	1/11/73	
Stack Effluent:				
Flow rate, DNM^3/M	229.37	150.08	127.43	169.05
Water vapor - vol. %	14.0	10.0	12.0	12.0
CO_2 - vol. % wet	16.0	16.0	19.0	17.0
CO - vol. % dry	0.36	0.20	0.067	0.41
SO_2 - ppmv dry	31	38	47	40
H_2S - ppmv	<.10	<.10	1.7	0.6
COS - ppmv	15	1	<1	6.0
CS_2 - ppmv	13	2	1	5.7
NO_x - lb/hr	0.57	0.59	0.46	0.54
HC - lb/hr	0.90	0.44	0.21	0.52

Source: Reference 3

TABLE 4

FACILITY B
Summary of Results

Test Number	B1			
Run Number	1	2	3	Average
Date	3/5/74	3/6/74	3/7/74	
Stack Effluent:				
Flow rate, DNM^3/M	65.5	71.6	68.8	68.6
Water vapor - vol %	4.2	5.0	3.3	4.2
CO_2 - vol. % dry[a]	5.4	5.5	6.0	5.6
O_2 - vol. % dry[a]	0.6	0.5	0.3	0.5
CO - vol. % dry[a]	0	0	0	0
CO_2 - vol. % dry[b]	5.8	5.7	5.9	5.8
O_2 - vol. % dry[b]	0.02	0.09	0.02	0.04
CO - vol. % dry[b]	566	565	604	578
SO_2 - ppmv dry[c]	3.6	3.8	4.5	4.0
SO_2 - ppmv dry[d]	1.5	0.7	0.76	1.0
COS - ppmv dry[d]	17	17	15	16
CS2 - ppmv dry[d]	0.15	-	-	-
H_2S - ppmv dry[d]	<0.1	<0.1	<0.1	<0.1
TS - ppmv dry[d]	19	17	16	17
NO_x - ppmv dry[e]	1.1	0	0	0.4
THC - ppmv dry[f]	-	-	-	-
Visible emissions	0	0	0	0

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[a] Orsat analysis

[b] NDIR/Paramagnetic

[c] EPA-6

[d] GC/FPD (EPA-18)

[e] EPA-7

[f] Total hydrocarbons as methane by flame ionization

[g] EPA-9

Source: Reference 4

TABLE 5

FACILITY B
Summary of Results

Test Number	B2			
Run Number	1	2	3	Average
Date	3/5/74	3/6/74	3/7/74	
Stack Effluent:				
Flow rate, DNM3/M	-	-	-	-
Water vapor - vol. %	-	-	-	-
H_2 - vol. %	5.0	6.0	5.8	5.6
CO - ppm	479	620	595	565
CH_4 - ppm	125	206	332	221
N_2 - vol. %	87.7	87.0	86.9	87.2
O_2 - vol. %	0	0	0	0
H_2S - ppm dry	7	1	0	2.7
Ar - vol. %	1.0	1.0	1.0	1.0
CO_2 -vol. %	63	6.0	6.3	6.2
COS - ppm dry	9	9	9	9.0
SO_2 - ppm dry	0	0	5	1.7
CS_2 - ppm dry	0	0	0	0

Source: Reference 5

TABLE 6

FACILITY B
Summary of Results

Test Number	B3				
Run Number	1	2	3	4	Average
Date	7/10/74	8/8/74	9/24/74	9/24/74	
Stack Effluent:					
Flow rate, DNM^3/M	-	-	-	-	-
Water vapor[1] - vol. %	-	-	-	-	-
CO_2 - vol. %	-	-	-	-	-
CO - ppm	-	-	346	335	341
SO_2 - ppmv dry[1]	0	0	0	0	0
COS - ppmv dry[1]	23.0	16.0	6.8	7.0	13.0
CS_2 - ppmv dry[1]	9.7	0	0	0	2.4
H_2S - ppmv dry[1]	0	0	0	0	0

Source: Reference 6

Note:
1. Assume moisture level of 5.6% based on test B_2.

Table 7

FACILITY C
Summary of Results

Test Number	C
Run Number	1
Date	2/14/74
Stack Effluent:	
Flow rate - DNM^3/M	11.33
H_2S - ppmv[a]	197
H_2S - ppmv[b]	<10
SO_2 - ppmv[a]	0
SO_2 - lb/hr[b]	5.5
SO_3 - lb/hr[b]	0
NO_x - ppmv[b]	14
CO - ppmv[b]	1500
O_2 - Vol. %[b]	12.5
CO_2 - Vol. %[b]	-
HC - Vol. %[b]	-

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[a] Incinerator inlet

[b] Incinerator outlet

Source: Reference 7

Table 8

FACILITY D
Summary of Results

Test Number		(See below)		
Run Number	1	2	3	Average
Date	6/10/74	6/11/74	6/12/74	
Stack Effluent:				
Flow rate - DNM^3/min	421	431	414	422
Water vapor - Vol. %	30.9	37.7	39.0	35.9
CO_2 - Vol. % dry[a]	1.3	1.1	1.1	1.2
O_2 - Vol. % dry[a]	0.28	0.35	0.31	0.31
CO - Vol. % dry[a]	-	-	-	-
CO_2 - Vol. % dry[b]	1.5	1.6	1.8	1.6
O_2 - Vol. % dry[c]	0.1	-	0.1	0.1
CO - ppmv dry[b]	3240	2450	3140	2940
SO_2 - ppmv dry[d]	59	42	42	48
SO_2 - ppmv dry[e]	420	430	360	400
SO_2 - ppmv dry[f]	82	72	80	78
COS - ppmv dry[f]	132	77	133	114
H_2S - ppmv dry[f]	1190	1410	1950	1520
CS_2 - ppmv dry[f]	460	180	300	310
TS (1) - ppmv dry[f]	2310	1920	2760	2330
TS (2) - ppmv dry[e]	2390	2590	-	2490
TS (3) - ppmv dry[g]	2380	2540	2070	2330
NO_x - ppmv dry[h]	7.8	1.0	4.0	4.3
Visible emissions[i]	0	0	-	0

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[a] Orsat

[b] NDIR

[c] paramagnetic

[d] EPA-6

[e] DuPont Analyzer(includes elemental sulfur)

[f] GC/FPD (EPA-18)

[g] Meloy Analyzer

[h] EPA-7

[i] EPA-9

Source: Reference 8

Table 9

FACILITY E
Summary of Results

Test Number	E1
Run Number	1
Date	12/12/74
Stack Effluent:	
Flow rate, DNM^3/min	-
Water vapor[1]- Vol. %	-
COS - ppm dry[1]	5
CS_2 - ppm dry[1]	0.5
H_2S - ppm dry[1]	<1
SO_2 - ppm dry[1]	<0.4
SO_4 - ppm wet	2
H_2SO_4 - ppm wet	<0.3
TS[a] - ppm	8+
TS[b] - ppm	14
CO - ppm wet	250
NO_x (as NO_2) - ppm wet	1

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[a] Total of separately measured constituents

[b] Total as measured by sulfur detector (includes mercaptans)

Source: Reference 9

Note:
1. Assume moisture level of 5.6% based on test B_2.

Table 10

FACILITY F
Summary of Results

Test Number	F1
Run Number	1
Date	11/6/74
Stack Effluent:	
Flow rate - DNM^3/M	311.49
COS - ppm dry	15.2
CS_2 - ppm dry	0.1
H_2S - ppm dry	0
SO_2 - ppm dry	0
Total sulfur - ppm dry	15.4
CO - ppm dry	670

Source: Reference 10

References

1. Source Test Report No. 74-SRY-1, EPA Contract No. 68-02-0232, Task Order No. 34, Environmental Science and Engineering, Gainesville, Fla., March 1974.

2. Letter, Thron Riggs, Standard Oil Co. of California to C. Sedman, ESED, OAQPS, EPA, dated August 9, 1974.

3. Source Testing Section Report No. C-1895, Los Angeles County APCD, February 28, 1973.

4. Source Test Report No. 74-SRY-2, EPA Contract No. 68-02-0232, Task Order No. 34, Environmental Science and Engineering, Gainesville, Fla., March 1974.

5. Letter, George L. Tilley, Union Oil Company of California, to C. Sedman, ESED, OAQPS, EPA, dated August 26, 1974.

6. Source Testing Section Report No. C-2082, Los Angeles County, APCD, Dec. 27, 1974.

7. Source Test Section Report No. C-2104, Los Angeles County, APCD, April 25, 1974.

8. Source Test Report No. 74-SRY-4, EPA Contract No. 68-02-0232, Task Order No. 34, Environmental Science and Engineering, Gainesville, Florida, June 1974.

9. Source Testing Section Report No. C-2234, Los Angeles County APCD, Feb. 20, 1975.

10. Source Testing Section Report No. C-2226, Los Angeles County APCD, Nov. 6, 1974.

APPENDIX D

EMISSION MEASUREMENT AND CONTINUOUS MONITORING

D.1 EMISSION MEASUREMENT METHODS

A review of the literature revealed that four different analytical methods could be used for analysis of sulfur compounds: colorimetry, coulometry, direct spectrophotometry, and gas chromotography. Although these methods were developed in most cases for measurement of ambient air concentrations, this did not preclude their application to measurement of stack gas emissions.

Colorimetry. In this method a sample is bubbled through a solution which selectively absorbs the component or components desired. The solution is then reacted with specific reagents to form a characteristic color which is measured spectrophotometrically.

An example of a colorimetric method is the methylene blue method which involves the absorption of reduced sulfur compounds in an alkaline suspension of cadmium hydroxide to form a cadmium sulfide precipitate. The precipitate is then reacted with a strongly acidic solution of N, N dimethyl-P-phenylene-diamine and ferric chloride to give methylene blue, which is measured spectrophotometrically. Automated sampling and analytical trains using sequential techniques are available for this procedure. Inherent deficiencies for stack sampling applications however include variable collection efficiency, range limitations, and interference from oxidants.

Another colorimetric method is the use of paper tape samplers impregnated with either lead acetate or cadmium hydroxide. These compounds react specifically with H_2S to form a colored compound which can be measured directly with a densitometer. Tape samplers would not be appropriate for all reduced sulfur compounds unless they were first reduced quantitatively to H_2S. In addition, the range is limited, the method requires precise humidity control and suffers from light sensitivity, fading, and variability in tape response.

Coulometry. In this method a gas sample is bubbled through a solution containing an oxidizing or reducing agent (titrant). The concentration of the titrant in solution is buffered by the presence of a titrant precusor. Passage of an electric current through the solution causes the titrant precusor to break down, releasing additional titrant into solution. Consequently, as the titrant is consumed by reaction with specific compounds contained in the gas sample, an electric current is passed through the solution to maintain the titrant concentration. The electric current required is a measure of the reactive compounds in the gas sample. Normally, the titrant is a free halogen such as bromine or iodine in solution as an oxidizing agent, or a metal ion such as silver in solution as a reducing agent.

For determining emissions coulometric titration has the advantage of responding to a wide variety of sulfur compounds. The response to each compound is quite different, however, and this makes standardization and reporting of data difficult in many cases. In addition, the method suffers from high maintenance and requires frequent calibration to reduce drift to acceptable levels.

Spectrophotometry. Although infrared and mass spectrophotometric methods are well established analytical techniques, most of these methods are considered too expensive and time consuming for routine field applications. Two such methods however considered for field analysis of sulfur compounds at sulfur recovery plants were ultraviolet spectrophotometry and gas chromotography followed by flame photometric detection.

In ultraviolet spectrophotometry a gas sample is first mixed with air, then filtered and split into two streams. One stream passes through a catalytic oxidation furnace where sulfur constituents are oxidized to SO_2 and then through an optical cell where its absorbance is measured. The second stream passes through a reference optical cell. Since SO_2 strongly absorbs ultraviolet radiation, the difference in absorbance values between the two cells is an indirect measure of the non-SO_2 sulfur constituents in the sample stream. The system is capable of measuring SO_2 concentrations in the range of 10 to 2500 ppm.

In gas chromatography/flame photometric detection, a gas sample is first injected into an inert carrier gas flowing through a gas chromatograph column. As the gas sample is transported through the column by this carrier gas, the individual components are separated by selective adsorption/desorption on the column packing. Each gas component, therefore, leaves the column as an individual "band" separated on either side by a zone of carrier gas. A flame photometric detector is then used to determine the amount of each component present in the initial gas sample by measuring the light emitted from the excited S_2 species formed as the gases leaving the column are burned in a hydrogen flame. A narrow band-pass optical filter placed between the flame and the photomultiplier tube provides a high specificity ratio (30,000:1) between light emitted from formation of S_2 when sulfur components are burned and light emitted from formation of other compounds when non-sulfur components are burned.

The gas chromatography/flame photometric detection (GC/FPD) method was considered the most promising technique for monitoring the composition of gas streams at sulfur recovery plants. The UV analyzer described previously was also used to serve as an independent check on the accuracy of the GC/FPD. This instrument detects elemental sulfur vapor which is not detected in the GC/FPD system.

D.2 MONITORING SYSTEMS AND DEVICES

For determining SO_2 emissions two types of continuous analyzers have been used by EPA for short-term (from a few weeks up to 6 months) data gathering. These analyzers are described below.

One is the Dupont 464 Source Monitoring System. The cost of a complete system including sample collection, analysis, and strip chart recording is in the range of \$17,000-19,000. Automated data reduction can be added at additional cost. A number of companies manufacture analog to digital converters in the price range of \$2,000-\$4,000 suitable for conversion of the 4-20 milliamp output of the Model 464 to a ppm SO_2 readout. The DuPont 464 system is a semicontinuous ultraviolet analyzer which responds to both SO_2 and elemental sulfur. Since the response to elemental sulfur is about seven-fold that to SO_2, SO_2 cannot be analyzed by this method if appreciable elemental sulfur is present. The Model 464 has not yet been used as a continuous monitor in sulfur recovery plants.

Gas chromatography/flame photometric detection (GC/FPD) is another method for monitoring SO_2 emissions. Systems using this principle include the Bendix Model 8700, Tracor Model 250H. These systems cost about the same as the DuPont 464 system discussed above and are also semicontinuous in operation. Recently, however, one vendor announced a complete sampling, analysis, and recording system for $14,000 (Tracor Model 270H). Again, automated data reduction can be added at additional cost. Integrators compatible with GC analyzers can be programmed to print the concentration of each sulfur compound. Cost of these integrators is in the range of $3,000-$4,000.

The GC/FPD system has several advantages. It can separate and detect each individual sulfur compound. These systems are extremely sensitive, however, and require sample dilutions of 100:1 or more. This presents a potential source of error and frequent calibration is necessary to minimize such errors.

Other continuous monitoring instruments are commercially available. Many of these are summarized according to their capabilities by Nader et.al. (EPA-650/2-74-013). To date, however, they have not been evaluated for use on sulfur plants.

For montiroing emissions of total sulfur and H_2S, the two systems described previously can be used. The DuPont Model 464 ultraviolet analyzer is capable of oxidizing the gas sample and measuring all sulfur compounds including elemental sulfur as SO_2. This system, however, is not able to monitor H_2S emissions.

The GC/FPD system is capable of monitoring individual sulfur emissions (except sulfur vapor). Total sulfur can be determined by adding the individually measured components to the estimated sulfur vapor. Sulfur vapor may be calculated from the partial pressure of sulfur at the gas stream temperature. Since H_2S vapor is one of the compounds determined by GC/FPD, it can be reported separately.

Although continuous monitors are available to monitor emissions of reduced sulfur compounds, compliance with the monitoring requirements included in the standards will be delayed until EPA promulgates performance specifications for these monitors.

Since the standards specify that emissions must be determined at zero percent oxygen, continuous monitoring of the oxygen concentration in the tail gases discharged to the atmosphere is required. A number of systems are available to monitor oxygen concentration and performance specifications for these systems were promulgated by EPA in 40 FR 46268 on October 6, 1975.

D.3 PERFORMANCE TEST METHODS

EPA Method 18, "Semicontinuous Determination of Sulfur Emissions from Stationary Sources," has been prepared for use in determining compliance with new source performance standards at refinery sulfur plants. This method requires use of the GC/FPD system discussed above and utilized during the emission testing program. Specifications for the dilution system, calibration technique, and other instrumentation necessary to insure accuracy, precision, and reliability are contained in Method 18.

In lieu of Method 18, Method 6 may be used to determine compliance for sources that incinerate the effluent gas before releasing them to the atmosphere. Although Method 6 has not been applied to this type of source, the similarity to emissions from fossil fuel-fired steam generators indicates the method to be applicable here also.